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THE EFFECT OF TEMPERATURE UPON NITROGEN FIXATION BY AZOTOBACTER[1]

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The Azotobacter group is widely distributed. The literature contains an abundance of citations of their uniform distribution throughout the entire United States. Lipman and Burgess (12) and others have shown Azotobacter to be present in a large number of foreign soils. The occurrence of Azotobacter in soils of Java is reported by Groenewege (5); in Japan by Yamagata and Itano (18); in India by Hutchinson (7); and in Denmark by Weis and Bornebusch (17).

When the great climatic variations between these countries are considered, the ability of Azotobacter to meet environmental conditions is remarkable. Thus it is not surprising that various investigators have studied the optimum conditions for nitrogen fixation by these organisms. Berthelot (2) was among the first to recognize that nitrogen fixation is influenced by temperature. He concluded that nitrogen fixation occurred best at summer temperatures, between 50° and 104°F., and that it was immediately stopped by heating soil to 230°F. Thiele (16) claimed that although Azotobacter could fix small quantities of nitrogen under laboratory conditions, these temperatures might not be favorable under field conditions. Heinze (6) showed that although the nitrogen-assimilating organisms were most active between 20° and 30°C., they were able to fix appreciable quantities of nitrogen at temperatures of 8° to 10°C. Koch (9) obtained fixation of 3, 11, and 15.5 mgm. of nitrogen per 100 gm. of soil incubated at 7°, 15°, and 24°C. respectively. Krzemeniewski (11) and Lohnis and Westerman (14) claim that the optimum temperature for nitrogen fixation is 28°C., and that extreme limits are 9° and 33°C. Lohnis (13) inoculated 100 cc. of 1 per cent mannite soil extract with 10 gm. of soil and incubated it at different temperatures; 3.15 mgm. of nitrogen were fixed at 10–20°C.; 4.55 mgm. at 20–22°C.; and 4.27 mgm. at 30–32°C. Jones (8) gives the maximum temperature for Azotobacter as 55–60°C., and the minimum near zero.

Soil microbiological investigations were commenced at the University of Arizona in the spring of 1930. As rapidly as time has permitted, soil samples

[1] Contribution from the department of agricultural chemistry, Arizona Agricultural Experiment Station. The author gratefully acknowledges the assistance and advice of Dr. P. S. Burgess, professor of agricultural chemistry, who suggested this problem.

have been obtained from the principal agricultural sections of the state. Most of the soils examined have possessed a very active nitrogen-fixing flora and Azotobacter have been found to be present in over 90 per cent of the soils examined to date.

The soils of southwestern Arizona are subjected to intense summer heat, and the soil temperatures are high. In the first few inches of the soil, the temperature during the summer months is high enough to coagulate egg albumin. Children at play, often bury eggs in the surface soil, and the eggs are "baked" within a short time. Although there is probably no fixation in the first inch or so, the lower depths of soil are also subjected to fairly high temperatures. Unpublished results of Evans[2] show that the average annual temperatures of soil in the experimental plots on the university campus are approximately 29°C. at a depth of 4 inches, and 21°C. at 10 inches. In the summer months these temperatures are somewhat higher probably attaining a maximum of approximately 32°. at 4 inches.

The purpose of this paper is to compare the amount of nitrogen fixed by the known species of Azotobacter at different temperatures with the quantities fixed by species isolated from Arizona soils, under similar conditions.

EXPERIMENTAL

In the summer of 1930, some preliminary tests were made to determine the effects of temperature upon nitrogen fixation. One hundred cubic centimeters of Ashby's liquid medium was inoculated with 2 gm. of soil, incubated at various temperatures for 14 days, and then analyzed for total nitrogen by the modified Kjeldahl method. The results, which are given in table 1, show that there was considerable fixation at temperatures higher than those generally considered optimum. It was then decided to isolate the Azotobacter species and to compare their azofying power with those of pure cultures of the various species of Azotobacter.

The six species of Azotobacter described by Bergey (1) were obtained from culture collections (three from the American type culture collection and three from Dr. E. Pribram's Mikrobiologische Sammlung, Vienna); and the local species were isolated from soils which had shown an especially active Azotobacter flora by inoculating 1 gm. of soil into 100 cc. of sterile Ashby's liquid medium which contained a small excess of calcium carbonate. The flasks were incubated for several days at 28°C. and a loop of the film was transferred by a sterile inoculating needle to a sterile flask of tap water. Dilutions were made and plates were poured, using Ashby's agar medium. The plates were examined both macroscopically and microscopically. Typical Azotobacter colonies were transferred to Ashby agar slants and incubated.

Slides were prepared and the stained mounts were examined carefully to detect any contaminating organisms. It was necessary to replate some of these

[2] Evans, M. M., research assistant in plant pathology, University of Arizona. Private communication.

cultures several times in order to remove contaminating organisms. Seven pure cultures were obtained and were used in these experiments.

No attempts were made to identify these organisms. *Azotobacter chroococcum* was probably the most common form. Each culture was designated by a number, corresponding to the soil sample from which it was isolated.

Cultures 3-1 and 3-4 were isolated from cultivated soil near Tucson; 5A and 6B from a cultivated soil several miles west of Tucson, which contained a rather large amount of soluble alkali salts; 13 was isolated from a virgin soil in the Casa Grande Valley, 1½ miles northeast of Casa Grande; 50-C and 50-4 from a reddish sandy soil in Oak Creek Canyon, about 75 miles northeast of Prescott (Yavapai County).

Twenty-four hours prior to inoculation, the stock cultures were transferred to slants of Ashby agar containing 0.05 per cent KNO_3, and incubated at 28°C. At the end of 24 hours the slants were completely covered with growth. The cultures were examined microscopically before each inoculation. A small

TABLE 1

Nitrogen fixed by mixed soil cultures at different temperatures

(100 cc. Ashby's solution inoculated with 2 gm. soil)

SOIL NUMBER	10°C.	28–30°C.	35°C.	40°C.	45°C.	50°C.
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
I C	2.7	14.7	10.0	4.9	3.2	2.2
5 A	1.2	16.0	14.0	2.2	1.3	1.2
6 C	1.7	15.0	14.5	6.1	4.4	1.6
10 C	1.6	13.3	10.9	7.9	2.8	1.6
15	2.6	15.0	12.5	11.4	3.8	3.6
19 A	1.0	13.0	5.6	4.3	5.0	1.0

amount of these actively growing cultures were transferred to 10 cc. of sterile tap water, and after being shaken gently, 1 cc. of this suspension was used as an inoculum. Fuller and Rettger (3) have shown that the size of inoculum is unimportant as long as a sufficient seeding is obtained to give satisfactory growth.

In order to approximate soil conditions to a certain extent and to promote aeration without the difficulties of using sterilized soil, sand slants were used in these experiments. Krainskii (10) found that cultures of Azotobacter, when grown in Ashby's solution containing sand, fix two to three times as much nitrogen as do the same cultures growing in Ashby's solution. Greaves (4) cites similar increases when gypsum or soil is added to Ashby's medium; the increases are attributed to greater aeration in the cultures, and probably to colloids added.

Sand, which had been previously washed with steam, was washed several times with water, dried and sterilized in a hot air oven at 200°C. for 4 hours. One hundred grams of this sand was placed in a 500-cc. Erlenmeyer flask with

100 cc. of Ashby's solution and sterilized at 15 pounds for 15 minutes. When cool, these flasks were inoculated with 1 cc., of the bacterial suspensions, and

TABLE 2

Nitrogen fixed by pure cultures of azotobacter at different temperatures

(1 cc. of aqueous suspension inoculated into 100 cc. of Ashby's solution)

CULTURE	18°C.	23°C.	27.5°C.	30°C.	32.5°C.	35°C.	37.5°C.	40°C.	42.5°C.
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
A. agilis	6.0	11.1	11.6	11.3	12.6	10.5	4.9	2.0	1.6
A. vinelandii	3.5	7.2	9.6	11.5	10.8	8.8	2.9	0.3	0.2
A. vitreus	0.9	2.0	1.8	1.9	1.6	1.3	1.3	1.2	0.2
A. woodstownii	0.5	1.6	2.1	2.9	1.2	0.9	1.8	0.6	0.1
A. beijerinckis	1.9	5.1	8.1	7.4	8.3	1.5	1.0	0.5	0.6
A. chroococcum	0.9	3.5	5.4	6.1	9.0	8.9	1.7	2.8	0.5
3-1	0.5	9.2	8.9	10.5	11.4	9.2	10.4	9.3	0.9
3-4	1.4	7.4	9.2	8.7	10.5	9.2	9.3	10.2	0.5
5-A	0.4	7.6	9.7	10.4	11.2	9.1	9.5	9.3	0.6
6-B	0.4	7.5	8.4	9.9	10.3	9.5	9.4	8.7	0.2
13	0.6	6.1	10.4	10.9	9.9	11.8	7.7	5.8	0.2
50-C	1.6	6.3	9.3	9.5	11.5	10.6	9.1	10.4	0.2
50-4	1.4	6.9	8.7	8.6	10.5	8.7	6.5	3.2	0.2

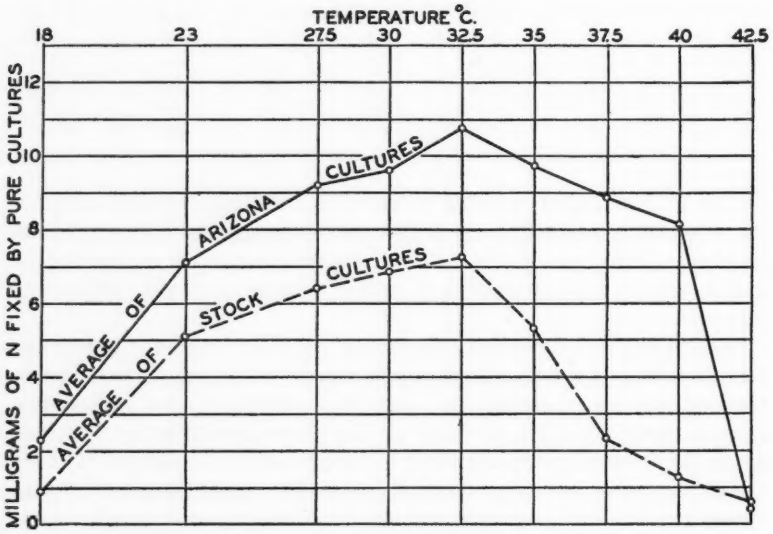

FIG. 1. THE EFFECT OF TEMPERATURE UPON NITROGEN FIXATION BY AZOTOBACTER

approximately 1 gm. of sterilized $CaCO_3$ was added. The flasks were whirled gently and then inclined at an angle of about 40°. In this manner a slant of

sand was formed which extended well above the surface of the liquid. Two flasks were inoculated from each culture and the flasks were incubated at the temperatures given in table 2.

The period of incubation was arbitrarily set at 14 days. Preliminary tests showed that at 28°C. most of the mannite was used up within a period of less than 8 days, and although larger amounts of nitrogen night have been fixed in a longer period of incubation, it was concluded that, in such a comparative study as this, 2 weeks would be sufficient time for incubation.

At the end of 14 days the cultures were carefully examined, and their appearance was noted (presence of film, pigment formation, etc.). The cultures were then shaken vigorously, allowed to settle a few seconds, and the solution was decanted to an 800-cc. Pyrex Kjeldahl flask. Thirty-five cubic centimeter of concentrated H_2SO_4 was added to each flask, and allowed to stand for 30 minutes with frequent agitation. The acid was then decanted into the Kjeldahl flask, and the sand remaining in the flasks was washed with 500 cc. of distilled water, using 50-cc. portions of water, shaking well, and then decanting off the liquid.

The excess of water was boiled off, and heating continued until charring commenced, then Hibbard's digestion mixture was added, and nitrogen was determined in the usual manner by the Kjeldahl method. In the first few series, blank determinations were made upon cultures inoculated in the same manner as the flasks which were incubated. The amount of nitrogen added in the inoculums could not be detected by the Kjeldahl method. In the succeeding series, blank determinations were made upon 100 cc. of the media only. The results of the analyses, from which the blank (0.1 mgm. per flask) has been deducted, are given in tables 1 and 2 and figure 1.

DISCUSSION

Tables 1 and 2 reveal several interesting facts. Table 1 shows that these soils have a very active nitrogen-fixing flora. The amounts of nitrogen fixed at 45° and 50° are significant, although it is doubtful whether fixation at these temperatures was due to Azotobacter, since film formation, which is characteristic of Azotobacter, was very slight at 40° and entirely lacking in some cases.

There is a great difference between the quantities of nitrogen fixed by the various Azotobacter stock cultures. Of these, *A. agilis* was by far the most active fixer, with *A. vinelandii* a close second; *A. beijerinckii* grew well from 27 to 32.5°C., and *A. chroococcum* was most active between 30 and 35°. It is also interesting to note that the greatest quantity of nitrogen was fixed at 32.5°, and that *A. agilis*, *vinelandii*, and *chroococcum* fixed considerable amounts at 35°, although the optimum temperature is considered to be 28°. *A. woodstownii* and *vitreus* were not active fixers at any temperatures.

The cultures of Azotobacter isolated from Arizona soils fixed less nitrogen at 18° than the stock cultures, but in the succeeding temperatures, the amounts were much greater. This is especially true at the higher temperatures. At

37.5° and 40° fixation is still very active, although the latter temperature is apparently the maximum for fixation under the conditions of these experiments.

There was not a great deal of variation in the amounts of nitrogen fixed by the Arizona cultures, as compared with the stock cultures.

It might be well for purposes of comparison to evaluate the temperatures used in terms of mean average temperatures of some cities. Smith (15) gives such a comparison. The mean annual temperature of Athens, Greece; Ft. Worth, Texas; Tucson, Los Angeles, and Buenos Aires is approximately 17–18°C. (63–65°F.); for Brawley, California, Mohawk, Arizona, and Rio de Janeiro, approximately 23°C. (73–75°F.); Yucatan and Khartum have mean annual temperatures of about 26°C. The record maximum for the United States is 57°C. (134°C.) in Death Valley.

TABLE 3

Average mean monthly temperatures of certain cities

CITY	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER	ANNUAL
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Boston	−2.2	−1.6	2.2	7.7	13.7	18.8	22.2	21.0	17.1	12.1	6.0	0	9.8
Chicago	−3.9	−2.8	2.2	8.8	14.3	19.9	23.3	22.7	18.8	18.2	4.9	−1.1	10.3
Sioux City	−7.7	−6.1	0.5	8.8	15.6	21.0	23.3	22.2	17.1	10.4	1.6	−5.0	8.2
Kansas City	−2.2	−0.6	6.0	12.6	18.2	23.3	25.5	25.0	20.4	14.3	7.1	0	12.3
Seattle	4.4	4.9	7.1	9.3	12.1	14.8	17.1	17.1	14.3	10.4	7.7	5.5	10.4
Maricopa, Ariz.	9.9	12.6	15.6	20.4	25.5	30.8	33.8	32.7	28.8	21.5	15.6	10.4	20.2
Prescott, Ariz.	0.2	3.5	6.3	9.5	13.2	18.2	22.2	21.0	17.7	11.5	6.6	1.9	11.1
Tucson, Ariz.	9.9	11.5	13.8	17.4	21.8	27.3	29.4	28.5	26.3	20.4	14.0	9.9	19.2
Yuma, Ariz.	12.4	14.7	17.6	20.9	24.6	29.1	32.6	32.5	28.9	22.5	17.3	12.6	21.9
Jerome, Ariz.	5.7	7.4	10.0	13.8	18.2	24.5	25.9	24.4	20.4	16.5	11.1	5.8	15.4

Three of the stock cultures were obtained from the northern part of the United States, and three from Vienna, where the mean annual temperatures are approximately 10° and 8°C., respectively, while four of the Arizona cultures were isolated from soils near Tucson, where the mean annual temperature is 18°C., and the extreme maximum and minimum are 45°C. and −14°C.; one from near Casa Grande where the mean annual temperature is slightly higher, and the extremes are 50° and −8°C. (112–17°F.). The two remaining cultures were isolated from soils in the lower Oak Creek Canyon, about 75 miles northeast of Prescott. Temperatures are not available for this district but the mean annual is somewhere near 17°C., with extremes of 45° to −14°.

Table 3 shows the average mean monthly temperature of certain cities of Arizona and other states. These figures, taken from Prof. Smith's bulletin (15), have all been converted to degrees Centigrade.

The temperatures are given for Maricopa because mean monthly average figures were not available for Casa Grande. The altitude of Prescott is 5,008

feet, which accounts for the lower temperatures. The temperature of Jerome, however, is nearer to that of Oak Creek Canyon, where samples 50-C and 50-4 were taken. The averages for Tucson and Yuma give some idea of the temperatures to which the soils of southern Arizona are exposed. It must be remembered that these are mean temperatures, and not extremes, which have been as great as 44.2°C. at Tucson, and 47.9°C. at Yuma. Table 3 shows that with the exception of Prescott, the temperatures of the Arizona cities are considerably higher for every month than the temperatures of the other cities.

It is apparent that the Azotobacter flora of Arizona soils have been subject to high temperatures for many thousands of years. In southern Arizona the lowest mean extreme maximum temperature, which is for the month of January, is 26°C., whereas during the months of May to September the mean extreme maxima vary from 37° to 41°.

It is not surprising, therefore, that these organisms are more active nitrogen fixers at high temperatures than are the stock cultures which were isolated from soils of more temperate regions. On the other hand, neither is it surprising that the latter were more active at lower temperatures. It does not seem, therefore, too far fetched to consider that these organisms have adapted themselves somewhat to their particular environment.

Objections may be raised to this assumption, but the fact remains that the stock cultures which were isolated from soils of temperate regions and which had been cultivated artificially for many generations on synthetic media at a temperature of 28°, far above the average temperature of the soils from which they came, did not fix as much nitrogen at higher temperatures as did those from Arizona soils, which are accustomed to higher temperatures.

Another objection is the possible loss of vigor due to prolonged cultivation under artificial conditions. Indeed, Fuller and Rettger (3) show that a freshly isolated strain of *Azotobacter chroococcum* fixed more nitrogen than did three stock strains of the same organism. This difference however, is not so great as the differences between the amounts of nitrogen fixed by the Arizona cultures and the stock cultures. Although it is possible, under certain conditions to attenuate some organisms, it is not possible to affect others materially. The typhoid organism may remain in a dormant state for a considerable period of time in ice cream, and yet a most virulent case of typhoid may result from some person eating that food. The Arizona cultures were isolated in October, 1930, and have been cultivated continuously on synthetic media since that time. These fixation experiments were not commenced until February, 1931, and were continued until August, 1931. Thus, any unusual vigor of a freshly isolated culture was avoided.

The life cycle of Azotobacter is short, but it has probably been so for ages. It does not seem possible, therefore, by means of cultivating these organisms for a relatively short time under entirely different conditions, to obliterate the effect of an environment that has lasted for a long period of years.

SUMMARY

The physiological activity of the six recognized species of Azotobacter has been determined at different temperatures. *A. agilis* is the most active nitrogen fixer, with *A. vinelandii* a close second. *A. beijerinckii* and *A. chroococcum* are next in order. *A. vitreus* and *A. woodstownii* were not active fixers at any temperatures.

The seven cultures of Azotobacter isolated from Arizona soils fixed greater quantities of nitrogen at all temperatures except at 18.0°C.

In general, greatest fixation occurred at 32.5°C. *A. agilis*, *vinelandii*, and *chroococcum* were quite active at 35°. Although the cultures from Arizona soils fixed the greatest amount of nitrogen at 32.5°, they were very active at higher temperatures. The quantities of nitrogen fixed by them at 40°C. were approximately the same as those fixed at 27.5°C. The maximum temperature for fixation was 40°C.

The Azotobacter flora of Arizona soils have been subjected to high temperatures for a long period of time. Data presented in this paper indicate that they have become adapted to this environment, and consequently are able to fix nitrogen at higher temperatures than cultures of Azotobacter which come from soils of more temperate regions.

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SORPTION PHENOMENA IN SOILS AND IN SILICA GELS

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The obscurity of many absorption and adsorption reactions, especially those occurring in soils, has led to a certain confusion in the use of terms: for this reason and to avoid the implication of any precise physical interpretation, the word "sorption" is employed in the present paper.

An attempt has been made to use conductivity measurements on soil-in-water suspensions to give a general and relative idea of the sorptive capacities of soils, correlating these observations with pH determinations. A comparison of natural soils was followed by observations on "hydrogen soils," on "calcium soils," and on pure silica gels in order that the specific effects of different ions might be compared and their part in the sorption mechanism elucidated. Similar determinations were made with soils previously heated through various ranges of temperature in order that further information (3) on the nature of changes thereby produced might throw light upon the process of sorption itself.

EXPERIMENTAL DETAILS

Conductivity measurements

The comparatively high resistances (specific conductivity of the order of 10^{-4} mhos) of soil in water suspensions (1 gm. soil: 5 cc. water) necessitated the use of large electrodes placed fairly close together; and, since stirring was necessary to ensure attainment of equilibrium, the electrodes had to be fixed securely in order that their relative position should remain unaffected. This condition was fulfilled by having small rods of borosilicate fastened across the corners of the electrodes, as shown in figure 1. Stirring was effected mechanically, using a stirrer of Pyrex glass made to move up and down outside the electrodes.

A number of Jena beakers served as conductivity cells: their rims were ground so as to give an air-tight fit with ground glass covers when not actually closed by the mahogany rubber-lined cover holding the electrodes. The whole arrangement is shown in figure 2.

All the conductivity measurements were taken at 18°C. The conductivity beakers were steamed before use. The cell constant (0.094) was checked from time to time, and remained invariable throughout the series of measurements.

[1] The author wishes to thank Mr. C. G. T. Morison, in whose laboratory the work was carried out and whose criticism and advice were invaluable.

The water used for conductivity and pH measurements was purified by boiling out distilled water in the Jena flasks normally used for storage, closing these before cooling with corks fitted to soda-lime tubes: It had an average specific

FIG. 1. RODS OF BOROSILICATE FASTENED ACROSS THE CORNERS OF THE ELECTRODES

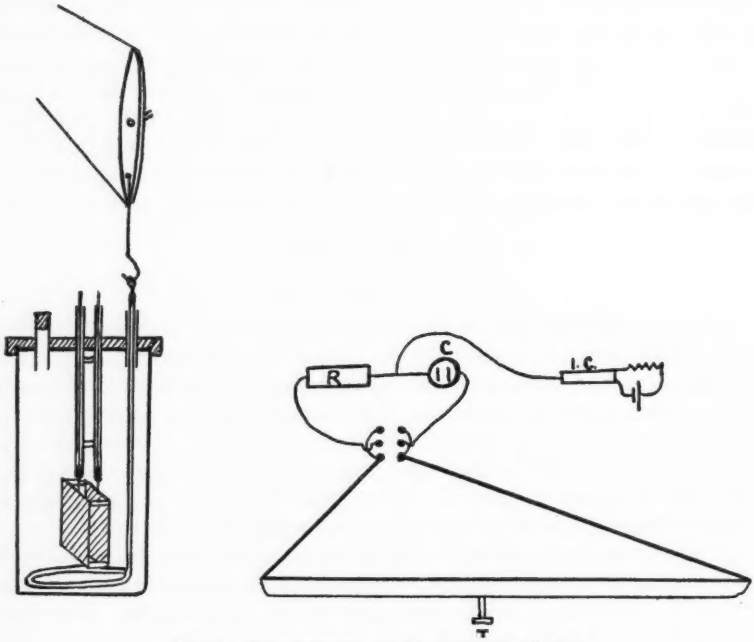

FIG. 2. ARRANGEMENT OF CONDUCTIVITY CELLS

conductivity of 1.6×10^{-6} mhos. All the salts used for sorption measurements were standardized conductometrically.

The 1:5 aqueous suspensions were made up in the proportion 30 gm. soil: 149.8 gm. (150 cc. at 18°C.) water, and stood in a thermostat at 18°C. It was

observed that mechanical stirring seldom altered the conductivity of suspensions which had been allowed to settle out overnight; and, in conductivity changes due to sorption, it was only necessary to stir for several minutes before an equilibrium value was attained. For the experiments on heated soils, duplicate 30-gm. lots were placed in weighed silica basins and heated in ovens at different temperatures: a few hours' heating to redness was sufficient to bring to constant weight but at 98°C. the weight altered gradually for several days and the heating was continued for a week. In order to obtain more strictly comparable results for soils which had lost a certain amount of water on heating, the aqueous suspensions were always made up with water to a weight of (30+ 149.8) gm., the excess water being allowed for in calculating conductivity due to added salts.

The conductivity of unheated soil-in-water suspensions showed a continuous drift, probably on account of bacterial action. Concordant initial values which remained constant over varying periods were attained by boiling the suspensions for a short time before use. The standard method finally adopted was to add to 30 gm. soil approximately 155 cc. water (to a mark on the outside of the beaker), bring quickly to the boil, keep boiling for 10 minutes, cool, and make up to a weight of (30 + 149.8) gm. This seemed to be the most accurate method attainable since it prevented bacterial action and, at the same time, gave values differing but slightly from those of suspensions kept at 18°C.

pH measurements

PH measurements and pH titrations were made on 1:5 aqueous soil suspensions using the quinhydrone electrode of Biilmann (1). Equilibrium pH values were reached almost instantaneously.

Determination of the "degree of unsaturation" (T-S)

The method of Hissink (5) was employed. Two-gram portions of soil were shaken with 50 cc. baryta solution of different initial concentrations and the final concentration of alkali was estimated after standing by titrating samples of the supernatant solution.

According to Hissink, the sorption of base from solution requires several days to reach equilibrium. On employing mechanical shaking, however, it was found that equilibrium hydroxyl concentrations were reached almost at once. Attainment of conductivity values which remained constant after the first 10 minutes on addition of KOH confirmed this conclusion.

Electrodialysis of suspensions

The dialysis cells were of the type designed by Mattson (8). The parchment membranes used in the first series of experiments were later replaced by cellophane paper. The electrodes were made as large as possible in order to minimize heating effects: the cathodes were made of fine nickel gauze and the anodes of platinized glass plates, made by fusing colloidal platinum into glass

at its melting-point. The P.D. across the cells was 100 volts and the maximum current about 0.2 amps.

The anode and cathode solutions were replaced after increasing intervals of time by distilled water. The total exchangeable cations were estimated as hydroxides, after addition of excess of standard acid, by titration. The anode dialyzates were titrated directly with 0.01 *N* KOH using methyl red as indicator: the total anions estimated in this way were only about one-eighth of the total cations: qualitative tests showed the presence of carbonate, nitrate, and sulfate; but no silicate ions could be detected in the anode solutions and were apparently unable to pass the pores of the parchment membrane.

It was found that small quantities of anions and cations continued to dialyze after an indefinite period of time; even two months of electrodialysis did not completely obviate further extraction.

The suspensions remaining after electrodialysis were washed into conductivity beakers and boiled as in the usual method. They were all extremely sticky: they had a pH of about 3.8 and a specific conductivity of about 0.5×10^{-4} mhos.

Five typical subsoils were employed. Their general characteristics are shown in table 1.

If no sorption or exchange reactions or other gel effect obtained, the specific conductivity of a suspension in *dilute* aqueous suspension should be the sum of two values:—the original specific conductivity and that of $x/(150 + x)$ *N* chloride solution, where x = cc. *N* chloride added to 150 cc. solution. Any variation from this calculated value would be due to the soil- or gel-complex.

After obtaining conductivity curves for addition of the salts to water only, preliminary tests were made with filtered soil and gel *extracts*. The calculated conductivity values were found to be identical with those obtained experimentally.

But, in cases of soil *suspensions*, a decrease in specific conductivity from the calculated value together with an increase in the acidity of the resulting solution was observed. This indicates that there is some kind of sorption from solution much greater in extent than the exchange reactions postulated by Page (10) and others. If the only reaction was a hydrogen exchange of the type MCl + H complex = HCl + M complex, the conductivity of the solution would increase, whereas exchange with other cations would have comparatively little effect. The decrease in conductivity due to sorption is therefore greater than that actually observed by an amount corresponding to the hydrion exchange.

The conductivity value observed about 10 minutes after each addition of chloride solution remained constant over periods varying from a few hours to several days, showing that the sorption, displacement, or whatever reaction it may be, is completed immediately.

Changes in specific conductivity and in pH on addition of various chloride solutions to all five soils are shown in table 2. It is seen from the table that, of the salts added, aluminum chloride gave the lowest final pH values; but, when

calculations were made to deduct acidity due to the salt solution itself, an actual decrease in hydrion concentration was found. Of the other salts added,

TABLE 1

Characteristics of the five subsoils used

SOILS	CLAY	$CaCO_3$	(T-S)	pH	SPECIFIC CONDUCTIVITY
	per cent	*per cent*	*m.e. per 100 gm.*		*mhos* $\times 10^{-4}$
I	33	...	32	4.6	1.40
II	56	...	36	7.5	2.81
III	9	0.1	15	7.8	1.03
IV	7.5	9.9	15	7.6	1.96
V	3.4	1.6	5	8.5	0.70

TABLE 2

(*B-A*) *values and final pH values for addition of chlorides to aqueous soil suspensions*

A = observed specific conductivity in mhos $\times 10^{-4}$.
B = calculated specific conductivity in mhos $\times 10^{-4}$.
N = normality of salt in mille-equivalents per liter.

N	2.5	5.0	7.5	10.0	pH	2.5	5.0	7.5	10.0	pH
	NaCl					KCl				
I	0.39	0.74	1.48	1.76	4.2	0.77	1.47	2.55	3.37	....
II	0.52	0.96	1.75	1.95	5.8	0.80	1.62	2.60	3.95	5.8
III	0.41	0.88	1.55	1.95	6.7	0.85	1.39	2.32	3.22	....
IV	0.47	1.03	1.82	2.30	7.2	0.65	1.26	2.14	2.76	....
V	....	0.80	1.15	1.33	7.8	0.58	1.15	2.07	2.71	....
	$MgCl_2$					$CaCl_2$				
I	0.32	0.52	0.88	1.39	4.0	....	....	....	1.69	4.0
II	0.35	0.64	1.06	1.51	5.7	0.70	1.22	2.0	2.88	5.5
III	0.50	0.88	1.29	1.78	6.5	....	....	.....	2.0	6.3
IV	0.47	0.82	1.24	1.65	7.1	....	.....	.....	2.32	6.9
V	0.35	0.70	1.14	1.69	7.1	....	....	.....	1.16	7.5
	$AlCl_3$					HCl				
I	....	0.98	....	2.31	....	6.4	11.4	15.7	.....	3.33
II	....	1.22	....	2.86	5.25	7.4	14.8	22.5	30.1	4.51
III	....	1.50	....	2.92	5.36	7.4	14.8	22.1	29.7	4.52
IV	....	0.66	....	1.79	6.8	7.0	14.2	21.5	28.8	6.55
V	....	0.68	....	0.4	7.1	5.8	12.7	19.8	27.0	7.14

displacement of hydrion was found to be greatest in the order Ca > Mg and K > Na.

When the conductivity decrease is plotted against calculated concentration

of added salt, regular curves are obtained. Soil II, having the highest clay content and showing generally greatest sorption, is taken as the typical soil for comparison of conductivity decreases in the different chloride suspensions. Figure 3 shows $(B\text{-}A)^v$ concentration curves for salts added to soil II.

In the subsequent comparison of sorptions for ordinary soils, no allowance is made for the slight increase in acidity resulting from these additions, since the $(B\text{-}A)$ values are at least one hundred times as great as the increases in conductivity due to hydrion exchange. (The decrease in pH is generally from about 7.5 to 5.5 in 0.01 N salt solution: this is a hydrion increase of only

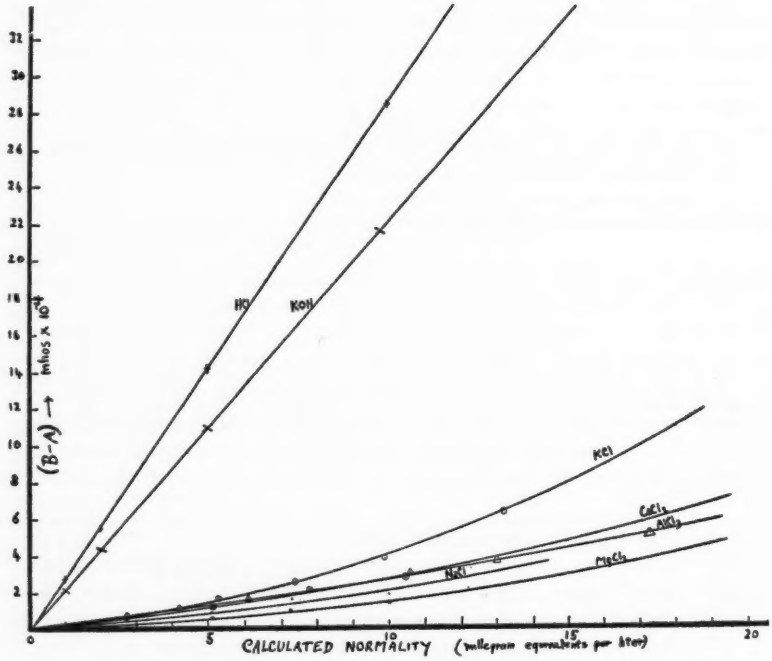

FIG. 3. $(B\text{-}A)^v$ CONCENTRATION CURVES FOR SALTS ADDED TO SOIL II

0.003 m.e. per liter, whereas the cation decrease, as noted from change in conductivity, is approximately 2 m.e. per liter.)

Neglecting exchange and therefore assuming equivalent sorption of anion and cation, the apparent decrease in salt concentration can be read off directly from suitable graphs of specific conductivity of aqueous salt solutions once the $(B\text{-}A)$ values are known. The results of this process for soil II are shown graphically in figure 4, from which it would appear that the cations have specific effects on the sorption process.

Table 3 gives a comparison of sorptions for the other soils as well: the order

of sorption for soil II is not exactly the same as that for the other soils, and must obviously be influenced by the exchangeable bases already present in the soil. In order to find the extent of this influence, a number of "hydrogen,"

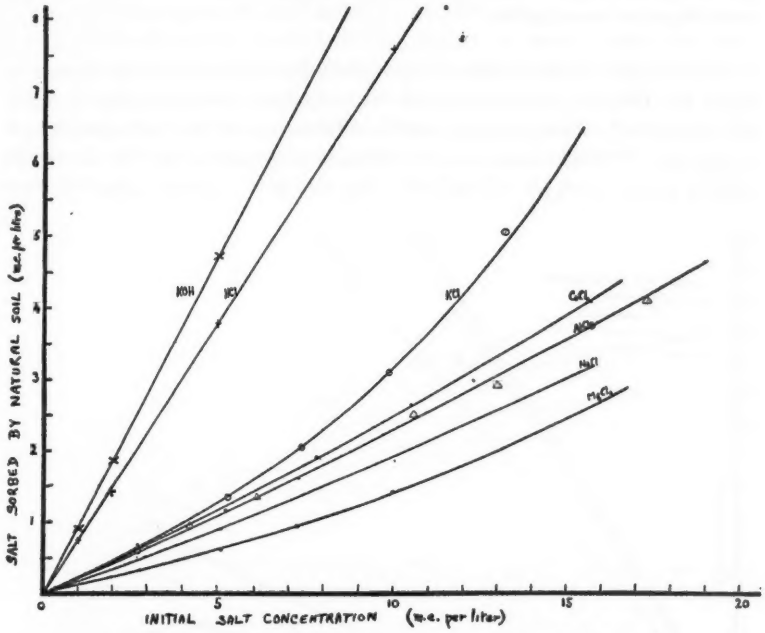

FIG. 4. SORPTION VALUES FOR A NATURAL CLAY SUBSOIL (SOIL II)

Explanatory note: The values plotted against *concentration* in this figure are *not* conductivity values: they are the actual *amounts* in m.e. per liter of the ions sorbed.—AUTHOR.

TABLE 3

Sorption values in m.e. per liter for solutions originally 0.01 N with respect to the salt added

SOIL	HCl	NaCl	KCl	$MgCl_2$	$CaCl_2$	$AlCl_3$
I	7.20	1.66	2.68	1.32	1.54	1.83
II	8.01	1.85	3.13	1.44	2.62	2.26
III	7.91	1.85	2.58	1.70	1.82	2.32
IV	7.67	2.19	2.19	1.58	2.11	1.42
V	7.20	1.26	2.15	1.62	1.05	0.31

"calcium," "potassium," and "sodium" soils were prepared and used for a similar set of sorption measurements: they were made by the following method:

Thirty-gram lots of soil II were boiled up with two successive portions of *N* chloride solution (0.2 *N* for HCl), the supernatant solutions being decanted through Whatman filters.

After six washings with distilled water, boiling up and draining off each time, almost the whole of the soil samples had been washed on to the filters. The sodium soils were so sticky that drainage of the wash water was very slow and only three washings could be given before filtration practically ceased. The samples were then washed off the filters into their original conductivity beakers, boiled, cooled, and made up to weight by the usual method. The loss of soil in the process was negligible.

Conductivity results obtained with previously leached soils are shown in figure 5. Those for the calcium soil were practically identical with those for the original soil, which probably contained 80 per cent of its exchangeable base as calcium. Potassium and sodium soils gave an apparent sorption of calcium slightly greater than the original soil: they also gave a greater apparent sorp-

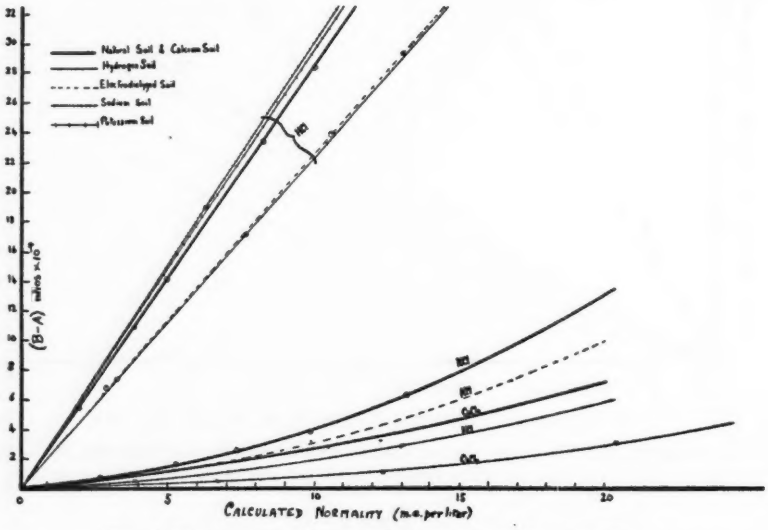

FIG. 5. CONDUCTIVITY RESULTS OBTAINED WITH LEACHED SOILS

tion of hydrogen. Hydrogen soils gave decidedly lower $(B\text{-}A)$ values and, at the same time, much greater increases in acidity than the original soils; e.g., for 0.01 N KCl an increase in C_H of 0.00055N was observed for the hydrogen soil in place of an increase of only 0.000002N for the untreated soil.

As the sorption was thus affected by the cations originally present in the soil, only the electrodialyzed and "hydrogen" soils were used to compare hydrion replacements. In parallel with the conductivity measurements on these soils, a series of C_H titrations was carried out, first obtaining "blank" C_H curves for addition of the salts to water only. The extra increases in acidity of the suspensions were then used to give C values, or increases in conductivity due to hydrion exchange: these values are shown in figure 6.

For an increase in hydrion normality of x, the C value would be found by subtracting the specific conductivity of x N MCl from that of x N HCl.

The values then tabulated were: $(B - A + C)$ = calculated decrease in conductivity due to sorption: S = sorption in milligram equivalents per liter as read off from conductivity v concentration curves.

The S values for the "hydrogen" soil appear in figure 7 and show that, despite specific effects on the displacement of hydrogen, there is, in the case of potassium, calcium, and magnesium, an identical sorption—or total removal of a particular cation—from solution. The greater slopes of the curves for aluminum and hydrogen would be expected to result from the greater acidity

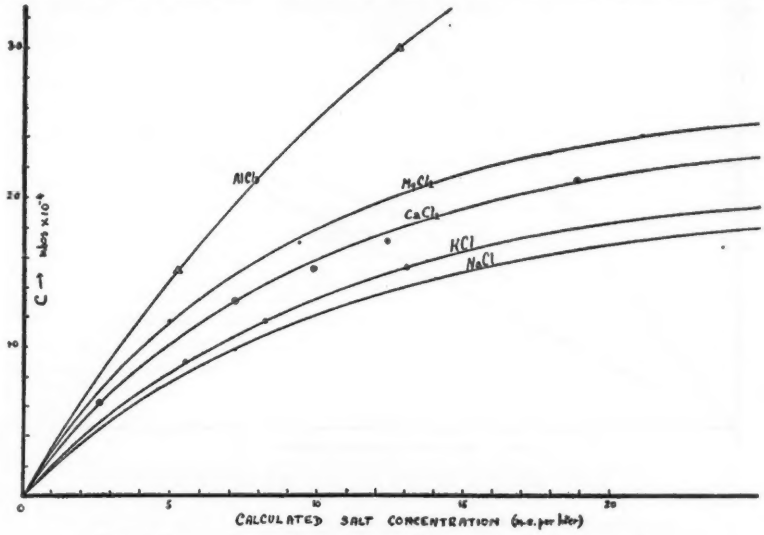

FIG. 6. INCREASES IN CONDUCTIVITY DUE TO HYDRION EXCHANGE

of the solutions if, as it appears, there is any kind of ratio distribution between soil and solution.

The curves for electrodialyzed samples of soil II showed sorption of hydrogen sodium, and potassium in equivalent amount and greater than that by the "hydrogen" soil. Now, the initial acidity of the suspensions of "hydrogen" soil, prepared by leaching soil II with hydrochloric acid, was greater than that of the electrodialyzed samples (pH about 3.3 instead of 3.8) and the hydrions in suspension would presumably compete in sorption with the metallic cations added. Thus the observed sorption would be less in the more acid solution. Such competition between cations has been noted by many investigators: for example, the calcium and potassium sorbed by hydrogels of silica and alumina have been shown to decrease with increasing hydrion concentration of the solution (4), whereas conductivity observations in the present series of experiments

on addition of potassium chloride following oxalic acid to soil-suspensions show that, for the concentration range 0.002 N — 0.05 N, the hydrion sorbed decreases with increasing concentration of potassium ions.

The next step was to observe the effects on conductivity, pH and sorption values of previous heat-treatment of all the natural soils, and to compare these values with the others. As already described, the samples were heated to constant weight: the suspensions were given an extra weight of water equal to the loss of "combined water" on heating.

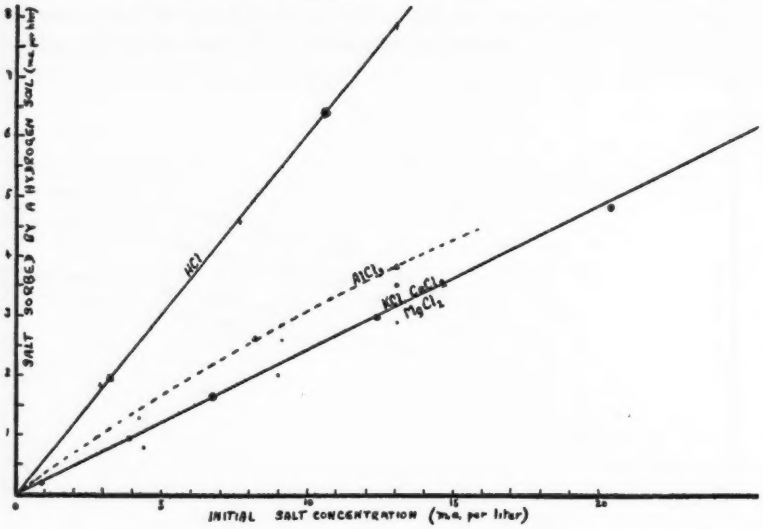

FIG. 7. SORPTION VALUES FOR THE "HYDROGEN" SOIL

TEMPERATURE EFFECTS

The effects of heating soils over various ranges of temperature are shown in table 4. A study was made of the resulting changes in specific conductivity, sorptive capacity as determined conductometrically, pH, and (T-S) values.

It is seen from the table that previous heating to 98°C. about trebles the specific conductivity of 1:5 aqueous suspensions: values for soils previously heated at 105–110°C. are greater than those for soils heated at 98°C., whereas heating at 150°C. increases the conductivity to an even greater extent. Ignition, except for the calcarious soils in which the enormous conductivity increases can be accounted for as due to formation of soluble oxides, decreases the conductivity to about half that for the unheated soils. The table shows a marked increase in acidity for suspensions of previously heated soils, indicating removal of hydrion from the colloidal complex of the soil.

It appears that, for each soil, there is an optimum temperature between the limits 110–150°C. at which the liberation of soluble salts from the complex is

greatest: it is at this temperature also that the sorption capacity (*B-A* values) for added cations and salts is greatest. These results indicate some kind of heat-activation of the colloidal soil complex.

In order to see whether the sorption problem for soils could be attacked in a more direct manner, it was decided to seek similarity between the conditions already described and those obtaining for colloidal silicic acid. For this purpose, three silica hydrogels were prepared by stirring solutions of hydrochloric acid into an equivalent amount of 2 *N* sodium silicate solution: they were

TABLE 4

Temperature effects on soils

TREATMENT	pH	A	S	pH	A	S	pH	A	S	pH	A	S	pH	A	S
	Soil I			Soil II			Soil III			Soil IV			Soil V		
Boiled	4.6	1.40	2.17	8.2	2.81	3.33	8.5	1.03	1.98	7.9	1.96	....	9.0	0.70	1.39
18°C.	5.0	1.06	2.59	7.9	2.40	3.39	8.2	0.74	2.31	7.6	1.21	....	8.8	0.46	1.90
98°	....	3.75	....	....	10.45	....	....	4.18	2.72	....	3.62	....	....	4.94	....
108°	3.9	3.56	2.42	6.0	11.60	4.30	6.8	5.97	2.72	7.1	7.95	....	7.2	7.40	2.93
120°	3.4	6.31	2.93	4.6	16.10	....	5.6	....	2.83	....	.....	....	7.0	5.39	3.58
160°	....	5.80	3.09	....	14.00	4.20	....	8.15	2.40	....	10.16	....	....	3.87	2.71
Ignited	5.5	0.93	1.57	....	2.74	1.55	6.0	3.00	2.06	11.0	.....	....	....	40.70	....

A = specific conductivity of 1:5 aqueous suspension in mhos $\times 10^{-4}$.

S = apparent sorption in mille equivalents per liter from 0.01 *N* KCl solution (neglecting corrections for changes in acidity).

TABLE 5

Properties of three gels

	APPROXIMATE COMPOSITION	H_2O	pH		SPECIFIC CONDUCTIVITY (10^{-4} MHOS)	
			1:5	1:50	1:5	1:50
		per cent				
Gel I	$SiO_2 \cdot H_2O$	23	....	4.20	...	0.20
Gel II	$SiO_2 \cdot 2H_2O$	37	3.72	....	1.1	0.15
Gel III	$SiO_2 \cdot 3H_2O$	47	3.74	4.64	1.6	0.22

washed by decantation, filtered off, forced through a dye onto gauze frames, and dried in a current of air at room temperature. The hard, glassy granules so obtained were purified by electrodialysis and then dried to constant weight at room temperature.

The three gels employed had the properties shown in table 5.

The gels were graded by sieving, the granules used being 1 to 2 mm. in diameter. Conductivity measurements on suspensions of particles of diameter less than 0.2 mm. gave the same values only when allowed to stand for some time after stirring: the presence of such particles between the electrodes increased

the electrical resistance of the suspensions. But, apart from this, particle size, and therefore surface area, had apparently no effect on the degree of sorption.

The conductivity and sorption values were unaffected by previous boiling.

Conductivity and pH titrations were made on aqueous gel-suspensions in a similar manner to those described for the soils; but the pH measurements had to be made on the "poured off" equilibrium solutions, as the presence of gel particles caused potential drift. It was therefore necessary to use a number of separate suspensions for each titration, withdrawing a fresh sample of solution for each pH measurement.

The three silica gels differed in the extent to which they liberated hydrions or sorbed cations according to their original composition. The gel prepared from

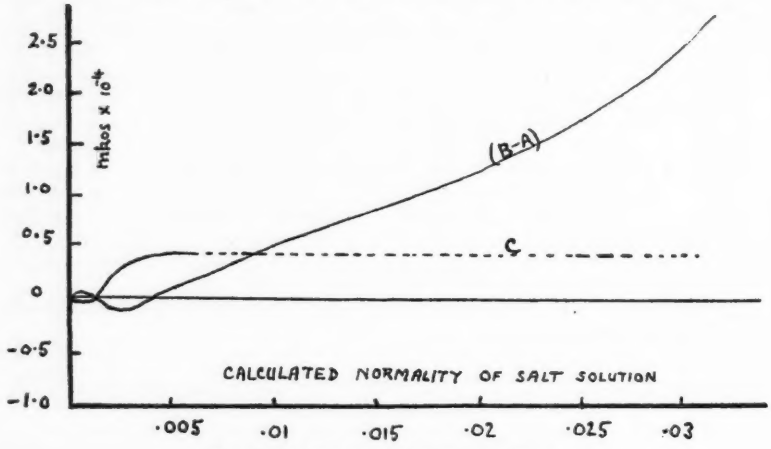

FIG. 8. (*B-A*) AND C CURVES FOR GELS

the weakest acid (0.5 *N*) and having the highest water-content showed least hydrion exchange but greatest sorptive capacity.

In addition to the usual chloride solutions, KNO_3 and K_2SO_4 were employed for conductivity and pH titrations, the concentration range being up to 0.05 *N*.

Attempts were also made to trace changes in chlorion concentration potentiometrically, using Ag: AgCl electrodes: they failed to yield concordant results. Such changes were estimated for 0.05 *N* solution by titrating the filtrates with 0.01 *N* $AgNO_3$, using di-chlor-fluorescein as indicator (6). Corresponding volumetric estimation of calcium, after precipitation as oxalate, showed removal of calcium and chlorine in equivalent amounts. But since the hydrion exchange or excess of cation to chlorion assumed to be removed from solution is only one-tenth of the total sorption in 0.01 *N* solution and also has greatest effect in the most dilute solutions, volumetric methods can hardly be relied on as a test of unequivalent sorption of anion and cation.

The gels gave greater exchange with hydrogen than the soils, the C values

being about one tenth of the (B-A) values for 0.01 N solutions. The relatively greater extent of hydrion exchange resulted in more complicated forms of (B-A) and C curves, which, although differing in extent according to the particular gel or cation used, were of the general form shown in figure 8. Though exaggerated for gel III, the figure underestimates the case for gel I, the gel giving the greatest hydrion exchange.

Below salt-concentrations of 0.002 N, very slight decreases both in acidity and in conductivity were observed, showing that addition of very small proportions of metallic cations can cause an increase in the sorption of hydrion from solution. With increasing concentration of salt, however, there followed a definite slight increase in conductivity accompanied by considerable increase in acidity, sorption being masked by exchange, until, in concentrations between 0.005 N and 0.01 N, there was little further hydrion exchange but an increasing sorption of ions from solution.

The two curves shown were combined to give ($B - A + C$) values, which were used to read off from the original "blank" curves the S values, or actual decreases in milligram equivalents per liter, of the particular cation employed. By this method, sorption concentration curves were obtained for all the salts and acids employed.

The only specific effects were those on hydrion exchange. The C_H curves varied in steepness according to the particular chloride on nitrate employed: displacement of hydrion was greatest in the order Ca > Mg > K > Na. The results for aluminum ions could not be compared with these because of the much higher proportion of hydrions present in aluminum chloride solution. Apart from the initial exchange reaction, no preferential order of cation sorption could be observed. The hydrions in solution must necessarily have a secondary effect on the sorption of any particular cation: the cation which replaces hydrogen to the greatest extent initially will be the most affected by competition with unlike ions.

The results obtained from conductivity and pH titrations on the 1:5 gel suspensions are given in table 6. Only the readings for gels II and III are included, partly for the sake of brevity and partly because the measurements for gel I were mostly taken on 1:50 suspensions instead of the 1:5 ratio employed in all the other cases. The 1:50 suspensions gave smaller sorption values with therefore a greater possible percentage error; otherwise there was no difference in the form of results obtained.

Table 6 shows that hydrion exchange in the gels has initially the greater effect on conductivity, whereas, with increasing concentration of salt, the predominating factor is removal of the salt as a whole. When the salt concentration has reached 0.01 N, most of the exchangeable hydrogen has been liberated: for potassium chloride, the C_H of gel II has increased from 0.00019 N to 0.00035 N, and that of gel III from 0.00018 N to 0.00025 N.

Although the final sorption curves resulted from a number of separate processes, they presented a remarkable uniformity. When sorption for any

TABLE 6

Addition of salts to 1:5 gel suspensions

N = normality of added salt in m.e. per liter.
A = observed specific conductivity in mhos $\times 10^{-4}$.
B = calculated specific conductivity in mhos $\times 10^{-4}$.
C = increase in specific conductivity due to hydrion exchange.
S = m.e. salt sorbed per liter (read off from conductivity graph).

	N	A	B	$B-A$	C	$B-A+C$	S	INCREASE IN C_H m.e./liter
				Gel III				
NaCl	4.2	5.79	6.09	0.30	0.09	0.39	0.37	0.04
	11.6	12.74	13.48	0.74	0.16	0.90	0.85	....
	15.9	16.63	17.67	1.04	0.18	1.22	1.15	....
	21.5	21.61	23.00	1.39	0.19	1.58	1.50	....
	29.9	27.11	29.05	1.94	0.19	2.13	2.02	....
	38.6	36.29	39.25	2.96	0.20	3.16	3.00	....
	44.8	41.41	44.91	3.50	0.20	3.70	3.55	0.07
KCl	5.5	8.16	8.48	0.32	0.13	0.45	0.35	0.04
	8.5	11.53	12.16	0.63	0.14	0.77	0.60	....
	11.3	14.71	15.59	0.88	0.15	1.03	0.81	....
	14.2	17.90	19.02	1.12	0.15	1.27	1.00	....
	18.8	22.88	24.27	1.39	0.16	1.55	1.22	....
	23.6	28.00	29.95	1.95	0.20	2.15	1.70	....
	26.8	31.38	33.58	2.20	0.21	2.41	1.91	....
	33.1	37.82	40.75	2.93	0.22	3.15	2.51	0.08
$MgCl_2$	2.2	3.81	3.81	....	0.12	0.12	0.11	0.04
	6.3	7.56	7.83	0.27	0.16	0.43	0.41	....
	8.8	9.77	10.26	0.49	0.17	0.66	0.62	....
	14.9	14.91	15.79	0.88	0.19	1.07	1.01	....
	20.4	19.62	20.75	1.13	0.20	1.33	1.27	....
	38.0	33.38	35.60	2.22	0.22	2.44	2.34	....
	46.5	23.65	42.72	2.90	0.23	3.13	2.98	0.07
$CaCl_2$	3.4	5.20	5.33	0.13	0.14	0.27	0.25	0.04
	6.1	7.82	8.12	0.40	0.15	0.55	0.49	....
	9.3	10.82	11.33	0.51	0.17	0.68	0.61	....
	12.2	13.40	14.13	0.73	0.17	0.90	0.81	....
	16.6	17.18	18.30	1.12	0.18	1.30	1.18	....
	36.6	34.11	36.50	2.39	0.20	2.59	2.36	....
	47.7	42.79	46.25	3.46	0.20	3.66	3.33	0.06
$AlCl_3$	9.1	15.28	11.49	−3.79	5.00	1.21	0.95	2.03
	13.2	19.71	15.80	−3.91	5.91	2.00	1.59	....
	18.2	25.23	21.00	−4.23	6.78	2.55	2.02	....
	25.6	32.24	28.45	−3.79	7.70	3.21	2.56	....

TABLE 6—*Continued*

	N	*A*	*B*	*B* − *A*	*C*	*B* − *A* + *C*	*S*	INCREASE IN C_H *m.e./liter*
Gel III—Concluded								
KNO_3	3.7	5.90	6.22	0.32	0.10	0.42	0.33	0.04
	8.4	11.03	11.66	0.63	0.14	0.77	0.65	....
	11.5	14.29	15.14	0.85	0.15	1.00	0.84	....
	17.4	20.54	21.74	1.20	0.16	1.36	1.14	....
	22.3	25.35	27.22	1.87	0.18	2.05	1.67	....
	30.8	33.87	36.29	2.42	0.21	2.63	2.16	....
	41.2	43.62	47.04	3.42	0.22	3.64	2.95	0.08
K_2SO_4	6.1	8.41	8.85	0.44	0.10	0.54	0.42	0.04
	8.9	11.30	12.07	0.77	0.12	0.89	0.71	....
	12.5	14.89	15.88	1.01	0.15	1.16	0.91	....
	33.0	34.11	36.75	2.64	0.17	2.81	2.27	0.08
HCl	2.7	10.54	11.65	1.11	....	....	0.30	....
	4.4	16.03	17.91	1.88	....	....	0.50	....
	6.9	24.17	27.08	2.91	....	....	0.78	....
	10.7	36.78	41.44	4.66	....	....	1.24	....
	15.1	50.60	57.76	7.16	....	....	1.90	....
	21.8	71.06	83.02	11.96	....	....	3.19	....
	27.4	88.41	104.41	16.00	....	....	4.26	....
	33.6	105.64	128.36	22.72	....	....	6.45	....
	42.3	132.10	162.44	30.34	....	....	8.08	....
Gel II								
NaCl	3.5	4.88	4.81	−0.07	0.28	0.21	0.20	0.11
	6.8	8.09	8.09	....	0.35	0.35	0.33	....
	12.2	13.21	13.45	0.24	0.40	0.64	0.60	....
	16.8	17.40	17.91	0.51	0.43	0.94	0.89	....
	24.5	24.36	25.18	0.82	0.45	1.27	1.20	....
	52.9	48.86	51.43	2.57	0.47	3.04	2.87	0.18
KCl	2.2	4.06	3.94	−0.12	0.27	0.15	0.12	0.11
	4.6	6.97	7.00	0.03	0.33	0.36	0.28	....
	10.9	14.29	14.64	0.35	0.38	0.73	0.57	....
	16.2	20.13	20.78	0.65	0.39	1.04	0.82	....
	23.4	28.00	29.16	1.16	0.40	1.56	1.18	0.18
$MgCl_2$	4.6	5.86	5.71	−0.15	0.37	0.22	0.21	0.18
	13.0	13.40	13.53	0.13	0.49	0.62	0.58	....
	18.8	18.32	18.64	0.32	0.52	0.84	0.79	....
	31.7	28.55	29.59	1.04	0.60	1.64	1.57	....
	37.1	33.24	34.38	1.14	0.60	1.74	1.66	....
	47.3	41.14	42.98	1.84	0.60	2.44	2.35	0.24

TABLE 6—*Concluded*

	N	*A*	*B*	*B* − *A*	*C*	*B* − *A* + *C*	*S*	INCREASE IN C_H
								m.e./liter
Gel II—Concluded								
$CaCl_2$	4.3	5.83	5.71	−0.12	0.45	0.33	0.30	0.18
	8.2	9.77	9.68	−0.09	0.53	0.44	0.40	....
	12.2	13.59	13.64	0.05	0.58	0.63	0.57	....
	18.5	19.41	19.63	0.22	0.62	0.84	0.76	....
	23.5	23.88	24.17	0.29	0.63	0.92	0.87	....
	40.4	38.52	39.35	0.83	0.63	1.46	1.32	0.24
$AlCl_3$	2.2	6.30	4.16	−2.14	2.75	0.61	0.47	....
	16.5	23.56	20.19	−3.37	6.11	2.74	2.18	....
	22.8	29.73	26.57	−3.16	6.90	3.74	3.06	....
	34.6	39.08	37.99	−1.09	8.16	7.07	5.70	....
HCl	1.5	5.98	6.53	0.55	....	....	0.15	....
	2.7	9.98	11.08	1.10	....	....	0.29	....
	5.7	20.25	22.05	1.80	....	....	0.48	....
	8.2	28.34	31.10	2.76	....	....	0.74	....
	12.8	43.91	48.70	4.79	....	....	1.28	....
	20.5	69.18	77.48	8.30	....	....	2.21	....
	24.7	83.26	93.62	10.36	....	....	2.76	....

particular gel was plotted against initial concentration of added salt, *straight line graphs resulted which, with the exception of the acids and aluminum salts, were identical for all the salts employed.* These results are shown in figure 9, in which the plotted points are all for gel III—the gel of least hydrion exchange but greatest sorptive capacity—while corresponding sorptions for gel II are shown by the dotted lines.

The results indicate equivalent sorption of Na, K, Mg and Ca. The coincidence of the graphs obtained for KCl, KNO_3, and K_2SO_4 indicates absence of anion influence. The greater sorption of Al and H by both soils and gels may be due to the greater acidity of the solutions. For the case of soils, where hydrion exchange was slight, there might possibly be an exchange with the aluminum of the soil-complex to as great an extent as that with hydrogen: the greater sorption of Al would then be in accordance with the partition coefficient distribution.

Addition of an aqueous solution of KOH to suspensions of soils and of gels caused rapid fall in conductivity to equilibrium values, indicating neutralization reactions or else comparatively great sorption. Whether hydroxl ions are only neutralized at the surface of the soil particles or are definitely adsorbed as stated by Mattson (7) and others, is questionable. Recalling the results of electrodialysis of soils, the author found the anions estimated by titration with alkali to be only about one-eighth of the total cations, no silicate ions being

detected in the anode chamber. Now, if hydroxlyion from the soil complex took part in conducting the current through the cells, it could not be detected as "adsorbed" hydroxyl ion since this ion is also liberated by the current in the cathode compartment.

Colloidal silica is said to have a negative charge in solution; and it seems possible that OH^- ions and replacing Cl^- ions are concentrated at the surface of the particles in accordance with some kind of membrane equilibrium which, however, is undisturbed by mechanical shaking.

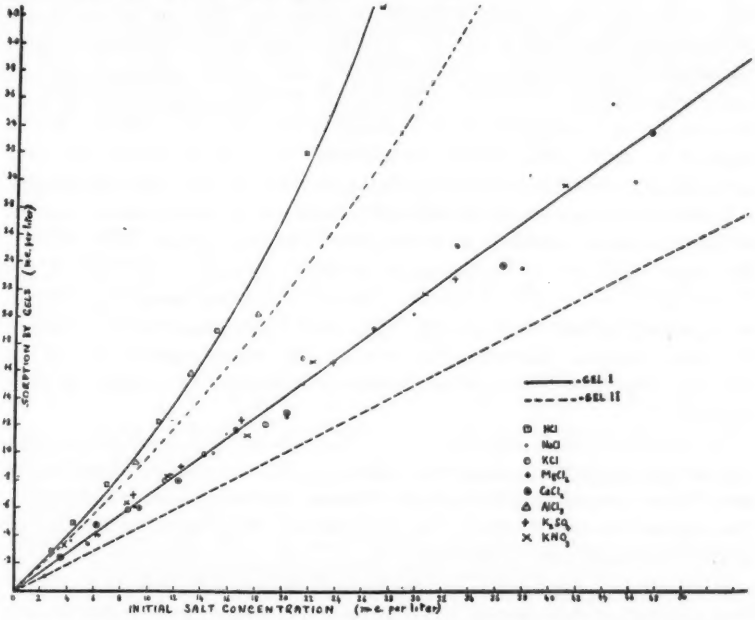

FIG. 9. SORPTION FOR GELS I AND II PLOTTED AGAINST INITIAL CONCENTRATION OF ADDED SALT

The effect of previous heating on the gels was quite different from that on soils. Samples of gel which had lost all their "combined" water on ignition gave out 30 heat calories per gram on wetting with water: after drying they had exactly regained their original water content and gave identical sorption values.

The analogy between soils and gels (2), however, must not be driven too far: comparison of temperature effects shows the soil complex to have a much more complicated structure.

DISCUSSION OF THE RESULTS

If the empirical equation of Freundlich holds, values of log a/log c, (where a = amount sorbed per unit weight absorbent and c = equilibrium concentra-

tion of solution) should give a straight line graph. For the sorptions here investigated and corrected for changes in acidity, this is the case.

If sorption of electrolytes is to be compared with that of non-electrolytes it must, according to Gibbs' condensation theory, correspond with the separate ionic effects on the interfacial tension and result from sorption of both ions individually. Adsorption of salts from solution has been studied chiefly with charcoals for which anion and cation are adsorbed to an equivalent extent, displacing ions of like sign in the order of their adsorbability which, for cations, is $H > Al > Ca, Mg > NH_4 > K$ and Na: acids and bases are adsorbed to a greater extent than their salts (11). Although sorption by charcoals is always equivalent, silicic acid and powdered iron oxide may adsorb anion and cation to a markedly different extent (9). Since accumulation of charge in the solution is impossible it is assumed on the exchange theory that the adsorbed ion is replaced by some other mobile ion liberated from the complex, and that unequivalent adsorption occurs only when a mobile ion is present in the sorbent.

In the present experiments on silica gel suspensions, a considerable increase in acidity was found invariably to result from addition of neutral salts between the ranges 0.002–0.01 *N* indicating an exchange reaction of the type $K^{\cdot} + Cl^{-} + H_2SiO_3 \rightarrow H^{\cdot} + Cl^{-} + K_2SiO_3$. But pH titrations showed this exchange to be greatest initially and to be very slight after a salt concentration of 0.01 *N* had been reached. Corresponding conductivity measurements showed an increased sorption of the added cation after all exchangeable hydrion had been replaced.

For concentrations of chloride below 0.002 *N*, a slight increase in alkalinity was sometimes observed: it appears, therefore, that very small proportions of metallic cations can cause an increase in the sorption of hydrion from solution. This explains the initial bend in the (*B-A*) curves which corresponds with that of the C curves, as shown in figure 8.

If the order of "sorbability" of the cations in silica gels is the same as that of their exchange with hydrogen, it is $H > Al > Mg$ and $Ca > K > Na$ which is the familiar order of valency, hydrion excepted. On the other hand, work on both gels and electrodialyzed, or "hydrogen," soils showed equivalent sorption of Na, K, Mg, and Ca, the word *sorption* meaning the *total* removal of cation both by exchange and by ab- or adsorption. The greater sorption of Al and H might simply be due to the greater acidity of the solutions.

The process involving removal of anions and cations from solution by soils and by silica gels is thus of a dual nature: the initial reaction is chiefly one of exchange but this is smaller in extent than the second process, which is probably removal of the salt as a whole.

SUMMARY

A study has been made of conductivity and pH measurements on aqueous suspensions of soils and silica gels, correlating the results with those obtained for samples which had been subjected to an initial heat-treatment.

Addition of neutral chloride solutions increases the acidity of soil and gel suspensions but effects a simultaneous decrease in conductivity. This shows sorption of ions in great excess to those taking part in "base exchange."

In the sorption reactions studied, there is immediate attainment of equilibrium.

Different cations are shown to displace hydrogen preferentially; but experiments on a "hydrogen" soil and on silica hydrogel show equivalent sorption of the cations Na, K, Mg, and Ca.

For five typical soils, an optimum temperature, between the limits 110°–150°C., was found to give maximum values for the acidity and conductivity of resulting suspensions and also for subsequent sorption of cations. For silica hydrogels, however, the effects appear to be completely reversible.

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AN IMPROVED METHOD OF MEASURING SOIL COLOR

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The method of measuring the color of a soil by comparison with a rotating disc composed of segments of black, white, red, and yellow paper was developed by Hutton and Rice of the Color Standards Committee of the American Soil Survey Association (1, 2). When this method is used the exposed portions of the four paper discs are altered until the blending of these when rapidly rotated gives a color comparable to that of the soil, which is held in a small dish or on a broad bladed spatula either over the rotating surface or closely beside it. Soils are granular, and even when they are carefully smoothed the diffusion of light reflected from the surface of the many particles, together with the shadows in the recesses of the soil, gives color values that are very hard to match.

A method of preparing and mounting the soil sample has been devised that permits of rotating the soil as the central part of the disc area thereby getting a mixed or composite light effect and color value that is very similar to that of the rotating color disc and which permits a much easier matching of the colors.

The soil is made into a suspension in about three times its volume of water, and is mixed until well dispersed. This mixing can be done by rubbing with the fingers or a rubber pestle or by boiling and pestling to destroy the aggregates. Usually it is well to let the soil stand for 12 to 24 hours after dispersing. The soil "mud" is then painted onto white blotting paper, using a small brush, and making sure that the blotting paper is so well coated that it does not show through the soil. When the soil-coated paper is thoroughly dry a disc 2 or 2½ inches in diameter is cut out, a hole punched in the center, and this disc mounted on the face of the color disc and fastened down by the lock nut (plate 1, fig. 1). It is well to use a washer of mounted blotting paper between the soil disc and the lock nut to prevent chipping and cracking the soil surface. When rotated the soil disc develops a smooth color effect similar to that of the color discs and a good match in color values is readily obtained (plate 1, fig. 2), As the soil disc is mounted on the inner circle of the disc assembly, comparison of the color effects is easy.

Nearly all soils will adhere to the blotting paper and bear considerable handling without the coating rubbing thin. Sandy soils are most difficult in this respect, although some of the heaviest clays have a tendency to crack

and the shadows in the cracks tend to give a darker shade. The color of the soil obtained by this method is essentially that of a dried and crusted soil or the surface of a dried clod, and may not truly represent the color effect of the granulated or broken soil surface as seen in the field. It is a natural color effect, however, and can be compared with other soils in the same condition. It can be readily reproduced with consistent measurement results, and affords a means of definitely measuring and comparing the color effects of soils.

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PLATE 1

THE SOIL COLORIMETER

FIG. 1. Colorimeter at rest with soil disc mounted in place. Exposed segments show black 69½, white14½, yellow 13, red 3.

FIG. 2. Colorimeter rotating. Match of color values is not exact, the soil disc showing slightly darker. Final adjustment gave black 71, white 14, yellow 12, red 3.

FIG. 2

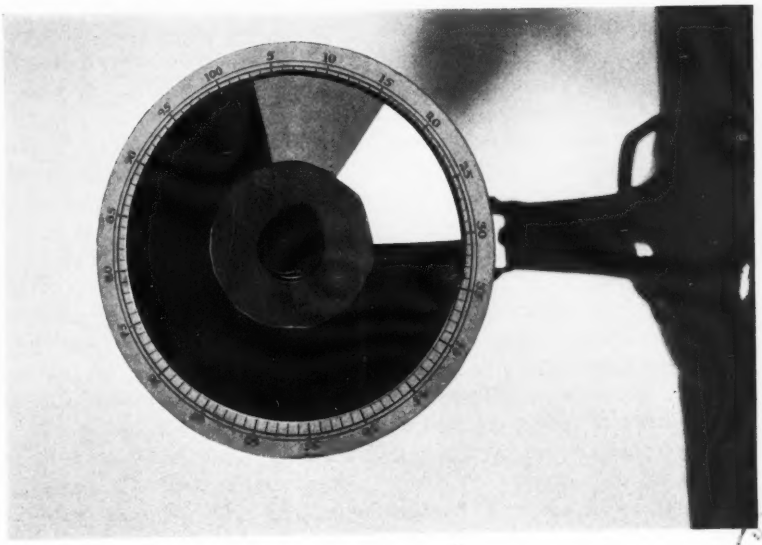

FIG. 1

U.S. DEPT. OF AGR.

FACTORS AFFECTING THE AMOUNT OF ELECTRODIALYZABLE IONS LIBERATED FROM SOME SOILS

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In an earlier paper (10) the author gave a description of the method and apparatus used in liberating the exchangeable cations from soils by electrodialysis. As the principle of electrodialysis has been adapted more and more into the field of soil investigations, a study of the factors which influence the ion exchange process is desirable. Of special interest is an investigation of the conditions affecting the speed of the replacement of ions which takes place in the soil suspension.

The author believes that the various conditions influencing the amount of ions given off from soils by electrodialysis should be accurately controlled in order to get reproduceable results. Then the results would give more information about the problem studied, and the data presented of various investigators should be much more comparable.

An important investigation as to the apparatus and technique of electrodialysis applied to the study of soils has just been reported by Odén and Wijkström (13). Of the data presented in this paper the most interesting in this connection are those which deal with the influence of temperature on the speed of the liberation of ions. The authors have found that increases in temperature cause only a slight increase in the quantity of exchangeable cations liberated, whereas the weathering effect on the soil particles is greatly increased. The influence of the temperature differs for different soils and for the various cations; the numbers given show that the increases in cation liberation per degree Celcius vary from 0.02 to 2.5 per cent for the replaceable cations and from 0.7 to 11.0 per cent for the quantities of the liberated cations which are supposed to descend from weathering effect or breaking down of the soil particles.

This paper deals with the study of the amounts of ions liberated and the speed of ion liberation from certain soils in relation to the concentration of the soil suspension used, to the distance between the electrodes, to the effect of increased voltages, and also to the influence of different membranes. These factors vary frequently in different experiments and it is believed that data which illustrate the influence of the mentioned factors will be of interest.

[1] The present investigation was made by the writer while at Cornell University and Ohio State University as a Fellow of the Rockefeller Foundation.

Comparison between the amounts of replaceable cations found by electrodialysis under various conditions and the amounts found by extraction with a neutral salt solution is also made.

SOILS AND METHODS USED IN THE INVESTIGATION

Six soils were used in the investigation; three of these belong to the Volusia silt loam type and three to the Ontario loam type. The chemical composition of these soils has been determined by Bizzell (3), and his analytical data are given in table 1.

The numbers in table 1 refer to the total amounts of the elements studied calculated in percentage of dry soil. The samples were collected to a depth of 8 inches, had passed through a sieve containing circular perforations 1 mm. in diameter, and then were pulverized in an agate mortar to a very fine powder (100 meshes to 1 linear inch) before the analytical procedure took place.

TABLE 1

Chemical analysis of the soils used in the investigation

(After Bizzell)

LABORATORY NUMBER	SOIL TYPES	CONSTITUENTS IN SOIL, DRY BASIS					
		Nitrogen	Phosphorus	Sulfur	Potassium	Calcium	Magnesium
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
7A	Volusia silt loam	0.194	0.076	0.064	1.66	0.18	0.22
49A	Volusia silt loam	0.134	0.046	0.063	1.81	0.49	0.52
50A	Volusia silt loam	0.205	0.078	0.071	2.17	0.41	0.64
14A	Ontario loam	0.143	0.048	0.063	2.44	1.08	0.85
48A	Ontario loam	0.125	0.052	0.037	1.64	0.56	0.51
79A	Ontario loam	0.404	0.119	0.057	1.98	0.84	0.73

The mechanical composition of the mineral fraction in the samples was determined by the method of Atterberg (1) and the results are recorded in table 2. The table also gives the content of organic material as determined by the hydrogen peroxide method (14), the water content in air-dry soils, and the pH values determined by the quinhydrone electrode.

The samples used in the author's experiments were passed through a sieve with openings 1 mm. in diameter and the data given in table 2 and following tables have been calculated on dry-weight basis.

The experiments with Volusia silt loam were made with Bradfield's (6) modification of the three-compartment electrodialysis cell and the experiments with Ontario loam were, with one exception, made with the cell devised by the author (10). The conditions under which the different experiments were performed have been varied more or less as to the problem to be studied. Such changes will be noted separately in connection with the description of the experiments. In this connection it should be mentioned that all experiments were

supplied with effective stirring of the soil suspension, and that the temperature, unless it is especially mentioned, was controlled and held constant at 23–25°C. without incorporation of resistance in the electrical circuit. By such an arrangement the voltage between the electrodes is kept constant during the time of experimentation. Concerning the temperature control it should be stated that in the experiment with the Volusia silt loam soils no cooling system was required in order to hold the aforementioned temperature limits because these soils are poor in replaceable cations. In the experiments where the Ontario loam soils were used, however, the temperature in the middle chamber, without a cooling system applied, arose within a short time to about 40–50°C. By a cooling arrangement as described by the author (10) the temperature was easily held within the desired range by ordinary tap water.

In plate 1, fig. 1, is shown the author's electrodialysis apparatus.[2] Several

TABLE 2

Mechanical analysis, organic material, water content, and pH values of the soils used in the investigation

SOIL NUMBER	SOIL FRACTION <1.0 MM. (DRY BASIS)					WATER CONTENT	pH
	Mineral material				Organic material		
	1.0–0.2 mm.	0.2–0.02 mm.	0.02–0.002 mm.	<0.002 mm.			
	per cent	*per cent*	*per cent*	*per cent*			
7A	14.08	47.22	19.19	16.61	2.90	1.46	5.35
49A	16.26	55.40	16.35	9.67	2.32	1.43	5.60
50A	6.88	48.80	24.25	16.47	3.60	2.10	5.25
14A	14.68	37.80	28.75	16.20	2.57	1.87	7.50
48A	16.75	46.03	27.35	7.62	2.25	1.27	6.25
79A	9.59	50.43	25.10	6.88	8.00	2.83	7.40

kinds of stirring arrangements and stirring motors have been tried. A stirring motor which especially can be recommended is the type recorded as C. L. 2 from Bodine Electric Co., Chicago. Ammeter, voltmeter, and a knife switch have been incorporated in the electrical circuit.

The experiments have been performed as fractional electrodialysis. The procedure of such experiments is briefly: The dialysates in the end chambers are removed at certain intervals and the chambers are refilled with distilled water, while the fractions obtained can be used for determination of the ions liberated. At the same time as the end chambers are drained a small portion of the soil suspension can be removed from the middle chamber for various measurements. After the desired measurements of the soil portions are taken, they must be dried and weighed in order that the amount of soil remaining in the middle chamber can be calculated.

In most of the experiments which are reported here the length of the inter-

[2] The apparatus can be supplied by the Central Scientific Company of Chicago.

vals between each changing of the dialyzates have been 12 hours. A more frequent changing of the dialyzates would, according to Odén and Wijkström (13) facilitate the exchange process. The purpose of these experiments, however, has not been to remove the exchangeable cations as soon as possible in these particular cases, but to study the conditions which influence the speed of the reactions which take place.

The fractions from the end chambers were poured into 200-cc. volumetric flasks, filled to volume, and portions of 50 cc. were used for determinations of the total amounts of cations and anions liberated in the different intervals. The determinations were made by titration against HCl and NaOH, using methyl red and phenolphthalein as indicators respectively. The normality of the reagents used has been 0.1 *N* and 0.01 *N*.

Besides the determination of the amounts of electrodialyzable cations liberated under various conditions, an investigation concerning the amounts of replaceable cations determined by help of extraction with ammonium acetate was made. By reason of its neutral character and its significant buffer capacity around the neutral point, this salt should be very favorable for use in base exchange work because the solubility effect on the soil particles should be very small. Also for other reasons this salt has advantages, one of the most important for the following analytical procedure of the extracts might be the ease by which the ammonium salt can be expelled [*see* Schollenberger (15) and Schollenberger and Dreibelbis (16)].

The method of mechanical dispersion and extraction used has, with some modifications, been that described by Bouyoucos (4) and Baver (2). Twenty-five grams of fine soil (< 1.0 mm.) is placed in a 250-cc. beaker, then 100 cc. of normal $NH_4C_2H_3O_2$ solution is added and the suspension is stirred for 10 minutes by a motor driven stirrer (plate 1, fig. 2a). The sample is then poured over into a Buchner funnel and, according to Baver, leached with a new 100-cc. portion of the ammonium acetate solution. Suction is applied in order to facilitate the leaching process.

In order to get a uniform amount of filtrate from all soils the author has changed the leaching procedure of the method, and instead of washing the sample in the funnel with a new portion of 100 cc. acetate solution the filtration is continued till 200 cc. of filtrate is obtained. For this purpose a combined suction-volumetric flask, which is shown in plate 1, fig. 2b, has been made. Filtration by help of this type of flask has proved to go very rapidly in relation to that with the Witt's filter apparatus or with the filter flask of Erlenmeyer form.

The solubility effect on the soil particles due to leaching with ammonium acetate solution has been studied by continued washing of the original samples until, in all, four fractions of 200 cc. each were obtained from each of the six soils investigated. The content of water-soluble salts in the soils was also determined. In this case the samples were treated in the same way as with the ammonium acetate method, but instead of salt solution distilled water

was used as the solution agent. The amounts of exchangeable cations and water-soluble salts in the soils were, after evaporation of the filtrate with concentrated HCl and expelling of the ammonium salt, determined as total chlorides first by weight and then by titration of the chloride ions with 0.1 or 0.01 *N* $AgNO_3$ solution using potassium chromate as indicator. As a control, aliquots of the filtrates have been electrodialyzed and the amounts of cations liberated by the leaching process were determined by titration of the cathode water by 0.1 *N* HCl solution using methyl red as indicator.

INFLUENCE OF VARIOUS FACTORS ON THE RATE AND AMOUNT OF ION LIBERATION FROM SOILS

Difference in the concentration of the soil suspension

In fractional electrodialysis experiments the concentration of the soil suspension decreases from fraction to fraction. Thus it will be understood that it is necessary to start with a large soil sample in order to get sufficient amounts of ions for the analytical procedure in the last fractions. The results obtained for each of the various fractions and for the whole experiment will then be more significant.

The extent to which difference in concentration of the soil suspension affects the rate of replacement of ions has received but little attention. The subject should preferably be studied under conditions where the concentration remains constant during the experiment, and the problem investigated by using different sized samples suspended in a given volume of water. In tables 3 and 4 are presented a series of results dealing with the aforementioned problem.

These tables contain results of experiments with soils 49A and 50A, and involve a comparison of 25-gm. and 50-gm. suspended in a bulb of 110 cc. volume. The distance between the electrodes was 6 cm., the voltage 110, and parchment was used as membranes.

Columns 3 and 7 in the tables show the amounts of cations, calculated in milliequivalents (M.e.) per 100 grams of soil, liberated from 25-gm. and 50-gm. samples, respectively. It is seen that in the first fraction a greater amount of cations is given off per unit weight of soils in the case of 25-gm. samples than in the 50 gm. samples. In the following fractions, the opposite is the case because more cations are left per unit weight in the 50-gm. sample. In the end, however, the total amounts of cations liberated are about the same in the two experiments.

The amount of cations given off per hour is given in columns 4 and 8. As we see, the amounts drop down to a minimum below 0.010 M.e. in the latter fractions. In the experiment with soil 49A this low value is reached after 36 hours when a 25-gm. sample was used but 60 hours was required to reach this same value in the experiment with 50 gm. In the experiment with soil 50A, a similar tendency is seen; the low end value, however, is reached after longer periods of time, presumably because this soil is somewhat richer in exchangeable

cations, and may also have a stronger adsorbing capacity due to a greater content of colloids and organic matter (table 2).

TABLE 3

Cations and anions removed from soil suspensions of varying concentration in various periods of time—soil 49A

FRACTIONS	DIALYZATES CHANGED AFTER	EXPERIMENT WITH 25-GM. SAMPLE				EXPERIMENT WITH 50-GM. SAMPLE			
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil	
		Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour
1*	2	3	4	5	6	7	8	9	10
	hours								
a	12	2.474	0.206	0.538	0.030	1.689	0.141	0.342	0.029
b	24	0.444	0.037	0.234	0.020	0.875	0.073	0.165	0.014
c	36	0.206	0.017	0.140	0.012	0.347	0.029	0.159	0.013
d	48	0.085	0.007	0.109	0.009	0.198	0.017	0.100	0.008
e	60	0.069	0.006	0.084	0.007	0.161	0.013	0.104	0.009
f	72	0.057	0.005	0.083	0.007	0.090	0.008	0.104	0.009
g	84	0.057	0.005	0.093	0.008	0.092	0.008	0.097	0.008
h	100	0.073	0.005	0.118	0.007	0.093	0.006	0.099	0.006
i	125	.....	.....	.....	.....	0.148	0.006	0.163	0.007
Total.....		3.465	.....	1.219	.....	3.693	.....	1.333	.....

* Column no.

TABLE 4

Cations and anions removed from soil suspensions of varying concentration in various periods of time—soil 50A

FRACTIONS	DIALYZATES CHANGED AFTER	EXPERIMENT WITH 25-GM. SAMPLE				EXPERIMENT WITH 50-GM. SAMPLE			
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil	
		Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour
1	2	3	4	5	6	7	8	9	10
	hours								
a	12	2.926	0.244	0.730	0.061	2.239	0.187	0.609	0.051
b	24	0.707	0.059	0.243	0.020	0.980	0.082	0.176	0.015
c	36	0.324	0.027	0.114	0.010	0.483	0.040	0.091	0.008
d	48	0.247	0.021	0.108	0.009	0.265	0.022	0.073	0.006
e	60	0.133	0.011	0.099	0.008	0.219	0.018	0.065	0.005
f	72	0.124	0.010	0.091	0.008	0.112	0.009	0.062	0.005
g	84	0.101	0.008	0.085	0.007	0.086	0.007	0.057	0.005
h	100	0.088	0.006	0.104	0.007	0.083	0.005	0.081	0.005
i	125	.....	.....	.....	.....	0.122	0.005	0.125	0.005
j	150	.....	.....	.....	.....	0.112	0.005	0.122	0.005
Total.....		4.650	.....	1.574	.....	4.701	.....	1.461	.....

Concerning the liberation of anions it will be seen in the tables that the amounts given off are much less than the amounts of cations, and also that the size of the samples has but little effect on the quantities found in the different fractions.

Experiments with soil 79A comparing 50-gm and 100-gm. of soil suspended in a bulb of 550 cc. volume were also performed. For the sake of brevity the data are not given, but it should be mentioned that the results were similar to those already described.

The advantage of using small soil samples is clearly indicated from the experiments. On the other hand the size of the samples should not be reduced too much, because of heterogeneity of the soil, which might cause an increase in the analytical error. For ordinary analytical purposes 25 gm. of mineral soil and 10 gm. of muck soil should be recommended.

Difference in the distance between the electrodes

Three series of experiments are performed in order to illustrate the influence of differences in the distance between the electrodes on the rate of ion liberation. These experiments, however, are comparable only to a certain extent because an increase in the distance between the electrodes results in an increase of the volume of the bulb in which the soil sample is to be suspended. In other words two of the experimental conditions are changed at the same time, and these might have more or less opposite effects. It was assumed, however, that an increase in the electrode distance followed by increasing resistance in the apparatus would dominate over the decrease in resistance which may occur as a consequence of the dilution of the soil suspension.

The experimental conditions were the following: Samples of 50 gm. of soil 79A were suspended into bulbs of 110 cc., 450 cc., and 550 cc. volume; the corresponding electrode distances were 6 cm., 9 cm., and 12 cm., respectively. The voltage in all experiments was 110, consequently the differences in potential between the electrodes expressed in volts per cm. were 18.3 volt/cm., 12.2 volt/cm., and 9.2 volt/cm. in the different cases. The membranes consisted of parchment at the cathode and cellophane at the anode. It should be stated that the temperature regulation was not entirely effective during the first interval in the experiment with 6 cm. electrode distance (for a short time it arose to about 50°C.), and the corresponding fractions of anode and cathode water (the a-fractions) might show too large amounts of ions because a rise in temperature facilitates the liberation of ions [Odén and Wijkström, (13)]. However, in the remainder of the experiments, and in the experiments with 9 cm. and 12 cm. electrode distance the temperature was held within the required limits of 23–25°C.

The results concerning the replacement of cations are recorded in table 5. Columns 3, 6, and 9 give the total amounts in the different fractions, and columns 4, 7, and 10, the average amounts per hour per fraction. In addition, the amounts of cations liberated per volt/cm. are given in columns 5, 8, and 11.

In table 6 the corresponding data concerning the liberation of anions are presented.

As seen from the tables, increases in the electrode distance from 6 cm. to 9 cm., and from 9 cm. to 12 cm. are followed by significant decreases in the amounts of ions removed from the soil. These decreases are especially visible

TABLE 5

Influence of differences in the distance between the electrodes on the replacement of cations

FRACTIONS	DIALYZATES CHANGED AFTER	ELECTRODE DISTANCE 6 CM.			ELECTRODE DISTANCE 9 CM.			ELECTRODE DISTANCE 12 CM.		
		M.e. per 100 gm. of soil			M.e. per 100 gm. of soil			M.e. per 100 gm. of soil		
		Per fraction	Per hour	Per volt/cm.	Per fraction	Per hour	Per volt/cm.	Per fraction	Per hour	Per volt/cm.
1	2	3	4	5	6	7	8	9	10	11
	hours									
a	12	6.720	0.560	0.367	3.680	0.307	0.302	2.480	0.207	0.270
b	24	2.720	0.227	0.149	2.560	0.213	0.210	1.860	0.155	0.202
c	36	1.836	0.153	0.100	1.786	0.137	0.146	1.600	0.133	0.174
d	48	1.469	0.122	0.080	1.380	0.126	0.113	1.240	0.103	0.135
e	60	1.195	0.100	0.065	1.360	0.113	0.111	1.000	0.083	0.109
f	72	1.236	0.103	0.067	1.153	0.096	0.095	0.840	0.070	0.091
Total.....		15.176	.....	.....	11.919	.....	.....	9.020	.....	.....

TABLE 6

Influence of differences in the distance between the electrodes on the replacement of anions

FRACTIONS	DIALYZATES CHANGED AFTER	ELECTRODE DISTANCE 6 CM.			ELECTRODE DISTANCE 9 CM.			ELECTRODE DISTANCE 12 CM.		
		M.e. per 100 gm. of soil			M.e. per 100 gm. of soil			M.e. per 100 gm. of soil		
		Per fraction	Per hour	Per volt/cm.	Per fraction	Per hour	Per volt/cm.	Per fraction	Per hour	Per volt/cm.
1	2	3	4	5	6	7	8	9	10	11
	hours									
a	12	1.291	0.108	0.071	0.587	0.049	0.048	0.470	0.039	0.051
b	24	0.234	0.020	0.013	0.391	0.033	0.032	0.352	0.029	0.038
c	36	0.120	0.010	0.007	0.199	0.015	0.016	0.274	0.023	0.030
d	48	0.082	0.007	0.004	0.162	0.015	0.013	0.152	0.013	0.017
e	60	0.078	0.007	0.004	0.148	0.012	0.012	0.120	0.010	0.013
f	72	0.078	0.007	0.004	0.144	0.012	0.012	0.112	0.009	0.012
Total.....		1.883	.....	.....	1.631	.....	.....	1.580	.....	.....

in the first fractions. It will be understood that a comparison can be made with accuracy only between the first fractions, because the amounts of ions remaining in the soil suspension at the beginning of the later intervals have changed according to the different amounts removed during the first period. Therefore the later fractions are more or less incomparable, and only when this

circumstance is taken into account can these results give the correct information.

Difference in voltage

The requirement for a great potential difference between the electrodes can also be met by increasing the voltage, by which means the current arises. In laboratories where only 110 volt alternating current is available, direct current can be easily produced and a higher voltage obtained by use of a suitable motor generator set. In the experiments performed by the author a motor generator set furnished with a field rheostat was used for delivering direct current; by use of the rheostat the voltage could be regulated within the range of 80–250 volts. In all experiments the desired voltage was kept constant during the time of experimentation.

Three series of experiments were conducted in order to show the influence of an increased voltage on ion removal. Only two of these, namely, those with soils 14A and 79A, will be reported in detail.

Soil samples of 50 gm. were suspended in a bulb of 450 cc. capacity; the electrode distance was 9 cm. The voltages compared were 125 and 250 with the first mentioned soil, and 110 and 220 with the second soil. These give comparisons between potential differences of 13.9 volt/cm. and 27.8 volt/cm., and between 12.2 volt/cm. and 24.4 volt/cm., respectively.

The analytical data are given in tables 7 and 8. By comparing columns 3 and 7 (table 7) and 3 and 8 (table 8) it is seen that the replacement of cations is much faster with the higher voltage than it is with the lower one. As the voltage is increased from 125 to 250 volts, or from 110 to 220 volts without changing the electrode distance the potential difference is doubled, and it should seem reasonable that the amounts of cations removed from the soils would rise proportionately. The relation, however, is equal to about 1:1½ and not equal to 1:2, presumably because of the gradual increase in the resistance as the cations are removed from the suspension, an increase which will be more pronounced in the cases where the higher voltages are used, because the removal of ions has taken place to a greater extent. For a shorter interval the ratio might have been different.

The numbers given refer to the first fractions, which are entirely comparable. By calculating the amounts of cations liberated per volt/cm. for the a-fractions, the following relationships are found:

Soil 14A:
Potential difference 13.9 volt/cm. gave 0.437 M.e. per volt/cm.
Potential difference 27.8 volt/cm. gave 0.344 M.e. per volt/cm. } or 1:0.79

Soil 79A:
Potential difference 12.2 volt/cm. gave 0.301 M.e. per volt/cm.
Potential difference 24.4 volt/cm. gave 0.230 M.e. per volt/cm. } or 1:0.76

In the rate of anion liberation from the two soils the differences due to increasing voltage are less, which also must be expected since the total amounts

of anions removed from the soils are small compared with the amounts of cations.

The higher rate of ionic exchange as a result of increased voltage was also observed in the third series of experiments (with soil 48A), for which the data are not presented.

In connection with the results concerning the liberation of cations it ought to be mentioned that investigation made by Wilson (17) also shows an increasing effect on the rate of replacement by using high voltage in electrodialysis of soils.

It is of interest to note the tendency to a rise in the exchange of cations which takes place after some duration of dialysis of soil 79A, which is

TABLE 7

Influence of difference in voltage on the rate of removal of ions—soil 14A

FRACTIONS	DIALYZATES CHANGED AFTER	EXPERIMENT WITH 125 VOLTS				EXPERIMENT WITH 250 VOLTS			
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil	
		Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour	Per fraction	Average per hour
1	2	3	4	5	6	7	8	9	10
	hours								
a	12	6.080	0.507	0.720	0.060	9.560	0.797	0.764	0.064
b	24	5.192	0.433	0.210	0.018	6.668	0.556	0.270	0.023
c	36	3.167	0.264	0.183	0.015	2.245	0.187	0.217	0.018
d	48	1.836	0.153	0.139	0.012	1.188	0.099	0.176	0.015
e	60	0.779	0.065	0.115	0.010	0.840	0.070	0.146	0.012
f	72	0.666	0.056	0.141	0.012	0.710	0.059	0.147	0.012
g	84	0.636	0.053	0.102	0.009	0.538	0.045	0.143	0.012
h	96	0.639	0.053	0.094	0.008	0.450	0.038	0.140	0.012
i	108	0.516	0.043	0.086	0.007	0.454	0.038	0.136	0.011
j	120	0.436	0.036	0.074	0.006	0.456	0.038	0.132	0.011
Total.....		19.947	.....	1.864	.....	23.109	.....	2.271	.....

shown in table 8. This phenomenon has been observed previously [Odén and Löddesöl (12)], and is supposed to be a consequence of the increase in acidity in the soil suspension during the experiments, followed by a solubility effect on the soil particles. In the experiment where 110 volts is used this rise in cation exchange starts after 108 hours' dialysis, or when about 15 M.e. of bases and about 2 M.e. of acids per 100 gm. of soil are removed from the sample. In the experiment with 220 volts the rise in exchange velocity starts after 96 hours' dialysis or when nearly 20 M.e. of bases and 2.6 M.e. of acids are removed. The pH values of the suspension which were determined at the end of each second interval, however, are in both cases about 5.0 when the rising tendency is observed. As will be understood, the change in pH value of the suspension is not only affected by the amounts of cations liberated from

the soil, but also the amounts of anions removed must be taken into consideration. The final pH value for this soil seems to be about 3.90, which was reached in the experiment where 220 volts was applied.

According to Mattson (10a) the appearance of the cations in the cathode chamber is to a large extent affected by the hydrogen-ion concentration in the soil suspension as a result of which weak hydroxides, which at the beginning of the experiment were precipitated on the cathode membrane, are brought

TABLE 8

Influence of difference in voltage on the rate of removal of ions—soil 79A

FRACTIONS	DIALYZATES CHANGED AFTER	EXPERIMENT WITH 110 VOLTS					EXPERIMENT WITH 220 VOLTS				
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension	M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension
		Per fraction	Average per hour	Per fraction	Average per hour		Per fraction	Average per hour	Per fraction	Average per hour	
1	2	3	4	5	6	7	8	9	10	11	12
	hours										
79A*	...	.....	.....	.....	.....	7.40	.....	.....	.....	.....	7.40
a	12	3.680	0.307	0.587	0.049	....	5.600	0.467	1.017	0.085	....
b	24	2.560	0.213	0.391	0.033	6.60	3.444	0.287	0.522	0.044	6.95
c	36	1.786	0.137	0.199	0.015	....	2.371	0.198	0.407	0.034	....
d	48	1.380	0.126	0.162	0.015	6.15	1.772	0.148	0.208	0.017	6.15
e	60	1.360	0.113	0.148	0.012	....	1.755	0.146	0.171	0.014	....
f	72	1.153	0.096	0.144	0.012	5.95	1.476	0.123	0.148	0.012	5.70
g	84	1.123	0.094	0.125	0.010	....	1.364	0.114	0.136	0.011	....
h	96	1.082	0.090	0.121	0.010	5.25	1.598	0.133	0.146	0.012	5.00
i	108	0.971	0.081	0.106	0.009	....	1.845	0.154	0.158	0.013	....
j	120	1.308	0.109	0.114	0.010	4.90	2.052	0.171	0.169	0.014	4.45
k	132	1.584	0.132	0.137	0.011	....	1.802	0.150	0.185	0.015	....
l	144	1.624	0.135	0.154	0.013	4.65	1.451	0.121	0.215	0.018	4.15
m	156	1.700	0.142	0.174	0.015	....	1.090	0.091	0.218	0.018	....
n	168	1.570	0.131	0.153	0.013	4.40	0.956	0.080	0.167	0.014	3.95
o	180	1.282	0.107	0.146	0.012	....	0.819	0.068	0.149	0.012	....
p	192	0.972	0.081	0.115	0.010	4.15	0.632	0.053	0.117	0.010	3.92
Total.....		25.135	.....	2.976	.....	....	30.027	.....	4.113	.....	....

* Undialyzed soil.

into solution. At a certain degree of acidity in the middle compartment the respective cations become mobile and penetrate to the cathode chamber. This statement of Mattson's seems very reasonable in view of the fact that a slight precipitate of iron and aluminum hydroxides has been observed on the cathode membrane in some of the experiments conducted by the author.

Different membranes

The general advice for use of membranes in electrodialysis experiment is that negative membranes shall be used at the cathode and positive membranes at

the anode. The main reason for such an arrangement is that the penetration of ions is facilitated when the membranes have an electrical charge opposite to that of the ions which are transported to the respective electrodes. In other words, negatively charged membranes are more permeable for cations than they are for anions, and if we deal with positively charged membranes the permeability for anions is greater than for cations.

The influence of different membranes on the rate of migration of different ions by electrodialysis has been studied by Bradfield (6, 7) using solutions of different sodium salts as a medium. He found, by placing a negatively charged membrane (parchment) at the cathode and a positively charged membrane (hemoglobin-collodion) at the anode, that the movement of cations and anions from the middle compartment to the respective electrode chambers took place in about equivalent amounts, and that the reaction of the solution in the central compartment changed to only a small extent. By using negatively charged membranes on both sides, however, he found that the movement of cations was much greater than that of the anions, followed by an increase in the hydrogen-ion concentration in the middle chamber. By adding a suspension of electrodialyzed colloidal clay to different solutions of dialyzable salts, Bradfield found that the behavior of the anode membrane changed as the rate of the removal of anions was retarded, because a layer of negatively charged clay colloids was formed on the inside of the membrane.

By continued electrodialysis of a soil suspension a gradual change in reaction in the acid direction takes place as a result of the replacement of the adsorbed base cations by hydrogen ions. In the previous tables it is seen that the amounts of anions liberated from the soils are much less than the amounts of cations. This is only what we could expect since most of the cations liberated have been associated with the acidoid soil complexes which remain in the middle compartment because the membranes are impermeable to colloids.

The extent to which the kind of membranes affects the rate of liberation of ions from a soil suspension has been but little investigated. Odén and Wijkström (13) recommend parchment, which is negatively charged, as cathode membrane; and cellophane, which the authors state is positively charged, as anode membrane. Then the electroendosmosis which takes place in the system will support the movement of ions and the process will be facilitated.

In a series of experiments conducted by the author parchment has been used both as cathode membrane and anode membrane in comparison with parchment used as cathode membrane and cellophane as anode membrane. The influence of changing the anode membrane on the speed of anion and cation liberation in relation to the change in the hydrogen-ion concentration in the soil suspension was then investigated.

The results of experiments with soil 7A are given in table 9. Soil samples of 50 gm. were used and dialyzed in Bradfield's three-compartment cell for 150 hours with a voltage of 110. By comparison of the first fractions in the table it will be seen that the liberation of anions takes place to a greater extent when

the anode membrane consists of cellophane instead of parchment (columns 5 and 10), but at the same time the amount of cations is less (columns 3 and 8). The results indicate that cellophane is more permeable to anions than parchment and this behavior might be explained as a result of the different charge of the two kinds of membrane. The explanation for the greater quantity of cations liberated in the case where parchment is used as anode membrane must be that an accumulation of anions in the middle chamber, followed by a formation of acids, has caused an increased solubility effect on the soil particles. The pH determinations made in the soil suspension from interval to interval

TABLE 9

Influence of different membranes on the rate of removal of ions—soil 7A

FRACTIONS	DIALYZATES CHANGED AFTER	PARCHMENT BOTH AS CATHODE MEMBRANE AND ANODE MEMBRANE					PARCHMENT AS CATHODE MEMBRANE AND CELLOPHANE AS ANODE MEMBRANE				
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension	M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension
		Per fraction	Average per hour	Per fraction	Average per hour		Per fraction	Average per hour	Per fraction	Average per hour	
1	2	3	4	5	6	7	8	9	10	11	12
	hours										
7A*	...	.....	.....	.....	.....	5.35	.....	.....	.....	.....	5.35
a	12	1.454	0.121	0.365	0.030	5.05	1.414	0.118	0.446	0.037	5.20
b	24	0.341	0.028	0.132	0.011	4.70	0.322	0.027	0.166	0.014	5.00
c	36	0.269	0.022	0.106	0.009	4.32	0.251	0.021	0.099	0.008	4.90
d	48	0.144	0.012	0.104	0.009	4.30	0.177	0.015	0.088	0.007	4.72
e	60	0.144	0.012	0.098	0.008	4.28	0.097	0.008	0.073	0.006	4.58
f	72	0.051	0.004	0.093	0.008	4.22	0.089	0.007	0.064	0.005	4.36
g	84	0.054	0.005	0.089	0.007	4.20	0.071	0.006	0.059	0.005	4.32
h	100	0.044	0.003	0.098	0.006	4.20	0.053	0.003	0.072	0.005	4.23
i	125	0.068	0.003	0.113	0.005	4.20	0.093	0.004	0.108	0.004	4.25
j	150	0.065	0.003	0.104	0.004	4.18	0.074	0.003	0.100	0.004	4.23
Total.....		2.634	.....	1.302	.....	....	2.641	.....	1.275	.....	....

* Undialyzed soil.

(columns 7 and 12) seem also to indicate that anions must have been accumulated in the middle chamber to a certain extent during the first intervals when parchment was used as anode membrane, because the lower pH values found can hardly be due only to the slight amounts of cations which are removed. The end pH values as well as the total amounts of ions liberated were in both experiments about the same.

Experiments with soil 50A gave similar results as those stated for soil 7A. The use of cellophane as anode membrane had facilitated the dialysis of anions during the first interval but at the same time the amounts of cations were less than when parchment was used.

The total amounts of exchangeable cations in the soils 7A and 50A are very

low. In order to see the effect of cellophane compared with parchment as anode membrane also on alkaline soil rich in exchangeable cations experiments with soil 79A were performed. The conditions under which the experiments were carried out were the following: Samples of 100 gm. of soil were suspended in a bulb of 550 cc. volume, the electrode distance was 12 cm. and the voltage 110.

According to table 2, soil 79A is rather high in organic matter, which adsorbs and holds cations very strongly (12). It was assumed that the exchange veloc-

TABLE 10

Influence of different membranes on the rate of removal of ions—soil 79A

FRACTIONS	DIALYZATES CHANGED AFTER	PARCHMENT BOTH AS CATHODE MEMBRANE AND ANODE MEMBRANE					PARCHMENT AS CATHODE MEMBRANE AND CELLOPHANE AS ANODE MEMBRANE				
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension	M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension
		Per fraction	Average per hour	Per fraction	Average per hour		Per fraction	Average per hour	Per fraction	Average per hour	
1	2	3	4	5	6	7	8	9	10	11	12
	hours										
79A*	...	.....	.....	.....	.....	7.40	.....	.....	.....	.....	7.40
a	12	1.620	0.135	0.332	0.028	7.22	1.700	0.142	0.391	0.033	7.30
b	24	1.530	0.128	0.160	0.013	7.12	1.510	0.126	0.220	0.018	7.18
c	36	1.435	0.120	0.122	0.010	7.08	1.290	0.108	0.122	0.010	7.05
d	48	0.975	0.081	0.103	0.009	7.02	0.742	0.062	0.103	0.009	7.00
e	60	0.713	0.059	0.073	0.006	6.97	0.728	0.061	0.085	0.007	6.92
f	72	0.567	0.047	0.078	0.007	6.80	0.698	0.058	0.073	0.006	6.80
g	84	0.560	0.047	0.084	0.007	6.60	0.599	0.050	0.070	0.006	6.65
h	96	0.547	0.046	0.081	0.007	6.52	0.565	0.047	0.062	0.005	6.53
i	108	0.529	0.044	0.073	0.006	6.45	0.502	0.042	0.058	0.005	6.47
j	120	0.515	0.043	0.074	0.006	6.37	0.487	0.041	0.059	0.005	6.35
k	132	0.504	0.042	0.076	0.006	6.30	0.468	0.039	0.055	0.005	6.27
l	144	0.484	0.040	0.072	0.006	6.25	0.452	0.038	0.051	0.004	6.25
m	150	0.295	0.049	0.049	0.008	6.20	0.290	0.048	0.044	0.007	6.22
Total.....		10.274	.....	1.377	.....	....	10.031	.....	1.393	.....	....

* Undialyzed soil.

ity of ions from such a soil would be slow, and the conditions under which the experiments were set up, particularly the large samples and the long electrode distance in relation to the voltage, would assure a very slow rate of replacement. That was also especially desired in this case where the relation between the ion liberation and the change in reaction of the soil suspension should be studied.

The results are given in table 10. For this soil, also, the amounts of anions removed during the first intervals are greater in the case where cellophane is used as anode membrane (columns 5 and 10) than where parchment is used. Regarding the liberation of cations it is of interest to note that in the case of the most alkaline reaction the larger amount is found in the experiment with cello-

phane as anode membrane, but as soon as the reaction changes to about neutral or becomes acid a tendency in the opposite direction is observed (columns 3 and 8). The changes in the pH values are seen to be closely related to the amounts of ions removed from the suspensions (columns 7 and 12). The experiments have not been run long enough to reach the point of increased acidity where an increased replacement of cations take place (table 8). The somewhat greater quantities of ions found in the last fractions (the m-fractions) in relation to previous fractions are evidently a result of changing the dialyzates after a shorter period of time than usual (column 2).

TABLE 11

Influence of different membranes on the rate of removal of ions—soil 48A

FRACTIONS	DIALYZATES CHANGED AFTER	CELLOPHANE BOTH AS CATHODE MEMBRANE AND ANODE MEMBRANE					CELLOPHANE AS CATHODE MEMBRANE AND PARCHMENT AS ANODE MEMBRANE				
		M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension	M.e. cations per 100 gm. of soil		M.e. anions per 100 gm. of soil		pH of the soil suspension
		Per fraction	Average per hour	Per fraction	Average per hour		Per fraction	Average per hour	Per fraction	Average per hour	
1	2	3	4	5	6	7	8	9	10	11	12
	hours										
48A*	...	.....	.....	.....	.....	6.25	.....	.....	.....	.....	6.25
a	12	1.880	0.157	0.368	0.031	6.05	1.600	0.133	0.400	0.033	6.00
b	24	1.339	0.112	0.260	0.022	5.85	1.394	0.116	0.213	0.018	5.80
c	36	0.820	0.068	0.131	0.011	5.30	0.888	0.074	0.201	0.017	5.28
d	48	0.724	0.060	0.091	0.008	5.00	0.760	0.063	0.228	0.019	4.90
e	60	0.886	0.074	0.059	0.005	4.65	0.681	0.057	0.204	0.017	4.60
f	72	0.946	0.079	0.077	0.006	4.30	0.605	0.050	0.216	0.018	4.25
g	84	0.796	0.066	0.106	0.009	4.25	0.569	0.047	0.201	0.017	4.22
h	96	0.675	0.056	0.140	0.012	4.20	0.580	0.048	0.201	0.017	4.20
i	108	0.545	0.045	0.145	0.012	4.18	0.675	0.056	0.198	0.017	4.20
j	120	0.508	0.042	0.129	0.011	4.20	0.733	0.061	0.183	0.015	4.15
Total.....		9.119	.....	1.506	.....	....	8.485	.....	2.245	.....	....

* Undialyzed soil.

Two series of experiments were also performed where cellophane was used both as cathode and anode membranes compared with cellophane as cathode membrane and parchment as anode membrane. Samples of 50 gm. of soil 48A and 14A were dialyzed in the author's apparatus with a voltage of 250 for 120 hours. The experiments with the two soils gave similar results, therefore detailed data will be reported only for soil 48A.

Table 11 gives the experimental data. There seems to be but little difference in the amounts of ions liberated whichever of these two arrangements is used, but it ought to be mentioned that the removal of ions from the soil in both cases is very slow. This can be seen by the data in columns 4 and 6 and in columns 9 and 11, which give the average amounts of ions liberated per hour in the vari-

ous intervals. The numbers given in the columns mentioned show that the quantities of ions which are liberated from one interval to the other decrease very slowly. The reason for this must undoubtedly be the incorrect placing of the membranes.

Columns 7 and 12, which give the pH values at the end of each interval, show a very good accordance in the change of the reaction of the soil suspension in the two experiments. The final pH value for this soil seems to be about 4.20. These values were obtained with small samples taken out of the middle chamber containing the stirred suspension. It is of interest, however, that determination of the pH value of a suspension made of clay colloids which were transported toward the anode and precipitated on the anode membrane shows the pH-value 3.45 [Bradfield (5)].

In order to find the total amounts of ions transported from the suspensions by use of different membranes the corresponding amounts of cations and anions were added and the sums are shown in the following collocation. As will be understood, only the a-fractions are entirely comparable:

Soil 7A: Cathode membrane parchment, anode membrane parchment, sum = 1.519 M.e.
Soil 7A: Cathode membrane parchment, anode membrane cellophane, sum = 1.859 M.e.
Soil 79A: Cathode membrane parchment, anode membrane parchment, sum = 1.952 M.e.
Soil 79A: Cathode membrane parchment, anode membrane cellophane, sum = 2.091 M.e.
Soil 48A: Cathode membrane cellophane, anode membrane parchment, sum = 2.000 M.e.
Soil 48A: Cathode membrane cellophane, anode membrane cellophane, sum = 2.216 M.e.

The greater quantities of ions transported when cellophane was used as anode membrane indicate that this material should be preferred in comparison with parchment. The ammeter reading during the experiments also showed that the current rose to higher values and the maximum amperage was obtained after shorter periods of time, which indicates that the resistance due to the anode membrane itself was less in the cases where cellophane was used.

TOTAL AMOUNTS OF EXCHANGEABLE CATIONS IN THE SOILS USED IN THE INVESTIGATION

In table 12 are summarized results of experiments for the six soils which were used in the investigations. Only the experiments in which the replacement of the exchangeable cations was supposed to have been completed, or at least nearly completed, are reported in the table.

It is of interest to note that the influence of the different treatments is most pronounced in the beginning of the experiments, but little by little the amounts of cations liberated from the same soil tend to be of the same magnitude. The quantities of cations given off, however, increased as long as the experiments continued, and it is of interest to know at what time the process of electrodialysis of a given sample is finished. How far the final values in the table really represent the so-called exchangeable or adsorbed cations in the soils is therefore an open question which requires further examination.

It might here be desirable to call attention to the fact that the terms "ex-

changeable" or "replaceable" cations very often are used as designations for all the cations liberated from soils regardless of whether or not the sources are adsorbed cations or cations from easily soluble salts. In many cases, especially for soils from humid regions, the last mentioned part is small compared to the former, but if any, this amount presumably will be liberated in the beginning of the experiments. Also by the neutral salt extraction methods at least the water-soluble salts are involved in the amounts taken out by the

TABLE 12

Total amounts of electrodialyzable cations in the soils used in the investigation

SOIL NUMBER	DIFFERENCE IN THE EXPERIMENTAL CONDITIONS	TIME DIALYZED	M.E. CATIONS PER 100 GM. OF SOIL AFTER:					
			12 hours	24 hours	36 hours	60 hours	100 hours	150 hours
		hours						
	Volusia silt loam							
7A	Anode membrane parchment	150	1.454	1.795	2.064	2.352	2.501	2.634
	Anode membrane cellophane	150	1.414	1.736	1.987	2.281	2.474	2.641
49A	25 gm. sample	100	2.474	2.918	3.124	3.278	3.465	.....
	50 gm. sample	125	1.689	2.564	2.911	3.270	3.545	3.693*
50A	25 gm. sample	100	2.926	3.633	3.957	4.339	4.650	.....
	50 gm. sample	150	2.239	3.219	3.702	4.186	4.467	4.701
			36 hours	60 hours	96 hours	120 hours	144 hours	192 hours
	Ontario loam							
14A	Voltage = 125	120	14.439	16.054	18.995	19.947	.....	.....
	Voltage = 250	120	18.473	20.501	22.199	23.109	.....	.....
48A	Anode membrane cellophane	120	4.039	5.649	8.066	9.119	.....	.....
	Anode membrane parchment	120	3.882	5.323	7.077	8.485	.....	.....
79A	Voltage = 110	192	8.026	10.766	14.124	16.403	19.611	25.135
	Voltage = 220	192	11.415	14.942	21.380	25.277	28.530	30.027

* 125 hours.

leaching procedure, provided the soil has not been washed with water for a sufficient time beforehand.

Besides cations from eventually easily soluble salts the electrodialysis as well as the leaching methods are supposed to cause a solubility or weathering effect on the soil particles themselves, so that the results obtained also include more or less cations from more difficultly soluble salts and the soil complexes.

Most writers who deal with electrodialysis of soils claim that their experiments have been continued till a constant amperage is obtained, or to at least one hour after the dialyzate drained from the cathode chamber does not give a color with phenolphthalein. The solubility effect during the time of experi-

mentation is then not taken into consideration. Odén and Wijkström (13), however, point out the necessity of distinguishing between the exchangable cations and cations liberated by weathering, and have found that the last quantity follows closely the parabolic equation:

$$y = B + \beta\sqrt{t}$$

from the time the replacement of the adsorbed base cations is completed. The y in the formula is the total amount of cations in M.e. liberated from the soil, B is the supply of cations which are exchangeable and those which are present in the soil solution developed from soluble salts, t is the time in hours, and β represents the weathering velocity of the soil. The reported equation is tried and found valid for calcium, magnesium, potassium, and sodium; by addition of the single equations the total amount of base cations (Y) from the respective soils can be found.[3]

The amount of cations liberated as a result of solubility processes might increase during the time of dialysis as a result of the increasing acidity in the soil suspension, although the differences in quantities of ions liberated under somewhat different reactions are not found to be very great (cf. the membrane experiments). On the other hand, it should seem reasonable that the amounts would decrease with time since the previously most weathered particles and part of the particles disappear first and the unweathered minerals will be left. The easily soluble salts will go into solution and the cations removed from the soil suspension to the greatest extent in the beginning of the experiments. Taking these circumstances into consideration the electrodialyzable cations appear to consist of the adsorbed cations plus a smaller amount of cations successively liberated from soluble salts and by weathering effect on the soil complexes, and it might not be far from the truth to assume that the amounts which are liberated from the last mentioned sources are approximately the same from time to time during the whole experiment. If this quantity could be found and subtracted from the total amount the remainder should be the exchangeable cations.

When a point of minimum cation liberation is reached the amounts of cations which are still liberated from the soil suspension remain approximately constant from interval to interval (cf. previous tables). All these cations presumably are removed as a result of the dissolving processes which act in the suspension. If these processes have been acting as long as the experiment has run and to about the same degree of effectiveness the correction should be the average amount of cations liberated per hour, after a constant value per time unit is obtained, multiplied by the number of hours of the experiment. This product subtracted from the total sum should give the exchangeable cations. This correction is related to that of Hissink (8) in his extraction method where the amount of base cations found in the second liter of filtrate is subtracted

[3] Cf. also a previous paper by Oden (11) where this problem is discussed.

from the amount found in the first liter. The basis for this manner of proceeding in the Hissink's method is the assumption that the solution process goes on during the whole time of leaching to approximately the same extent. Compared with Odén and Wijkströms equation, and using the same symbols, the suggested correction will give a straight line instead of a parabola from the moment all exchangeable cations are removed from the soil, and the factor B will not compose the cations from the soluble salts (which here are included in the factor β), but only the adsorbed or exchangeable cations.

By examination of the tables giving the detailed results of the experiments it is found that only for soils 7A, 49A, 50A, and the high voltage experiment with soil 14A, are the points reached where the liberation of cations remains approximately constant during more intervals, and where at the same time ap-

TABLE 13

Total amounts of exchangeable cations in some of the soils studied

SOIL NUMBER	LENGTH OF EXPERIMENTS	FINAL CATION LIBERATION PER HOUR	CORRECTION	TOTAL AMOUNTS OF CATIONS IN THE SOILS	EXCHANGEABLE CATIONS	MEAN	REFERENCE TABLE NUMBER
1	2	3	4	5	6	7	8
	hours	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
7A	150	0.003	0.450	2.634	2.184	2.188	9
	150	0.003	0.450	2.641	2.191		9
49A	100	0.005	0.500	3.465	2.965	2.954	3
	125	0.006	0.750	3.693	2.943		3
50A	100	0.006	0.600	4.650	4.050	4.001	4
	150	0.005	0.750	4.701	3.951		4
14A	120	0.038	4.560	23.109	18.549	18.549	7

proximately constant amperage is obtained. A constant amperage should, to a certain extent, indicate that the amounts of cations transported from time to time remain constant. In the experiments with soils 48A and 79A it is evident that the points of constant cation liberation are not reached, facts which also were observed during the experimentation, since constant ammeter readings were not obtained before the experiments were finished. The correction can therefore be tried only on four of the six soils studied. The results of such a trial are given in table 13, and the numbers given in column 7 should be the amounts of exchangeable cations in the soils.

In figure 1 the relationship between cation liberation and amperage is shown for soil 14A. The time is plotted on the abscissae and the total amounts of cations liberated from time to time on the ordinates. The amperage during the experiment is also plotted on the ordinates. The amounts of cations are given in milliequivalents and the amperage in milliamperes.

The connection between approximately constant cation liberation and amperage is clearly indicated from the graph. The correction suggested can also be illustrated graphically. If a tangent, which coincides with the straight part of the curve, is extended to the y-axis this axis will be cut at a certain point. The distance from the origin to this point represents the exchangeable cations.

It must be pointed out, however, that the different cations are set free with different speeds during the time of electrodialysis (12). Therefore a correction which might afford some aid in the estimation of the total amounts of exchangeable cations is perhaps less useful for the single cations.

If the problem is an investigation and comparison of the amounts of readily

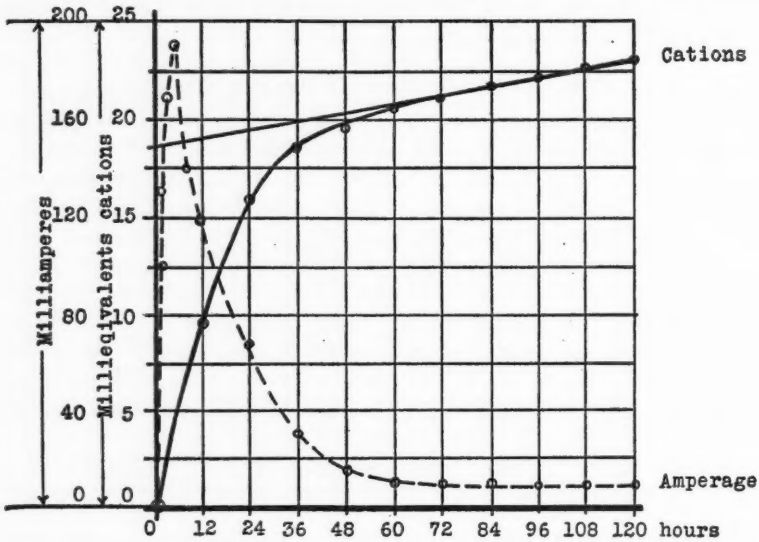

FIG. 1. RELATION BETWEEN CATION LIBERATION AND AMPERAGE

available cations from a number of soils a distinction between exchangeable cations and cations liberated by solution and weathering is of more theoretical interest than of practical value, because it is the total quantity of readily available base cations which indicates whether or not the soils are rich in plant nutrients. On the contrary, from the standpoint of comparison of the quantities of cations from different soils it is of great importance that the determinations are performed under similar and known conditions, such that the results obtained really are comparable.

In order to verify the results from the electrodialysis experiments the amounts of exchangeable cations in the soils were also, as previously mentioned, determined by extraction with ammonium acetate. These results are given in

table 14. The table gives also the amounts of cations from water-soluble salts in the soils.

As seen from the table the amounts of cations obtained by water extraction are small for all soils. The results of the ammonium acetate extraction show that leaching of the samples until 200 cc. of filtrate are obtained, such as proposed by Baver (2), has not been sufficient for these soils, especially for the soils which are rich in exchangeable cations (cf. soils 14A and 79A). This appears from columns 4, 5, and 6, which show that the second fractions of filtrate contain more cations than do the third and fourth fractions. For soils rich in replaceable cations the leaching procedure therefore apparently should be continued at least until 500 cc. of filtrate are obtained. It may also be seen from the data presented that ammonium acetate solution caused a slight solubility effect in the soils. In order to obtain the amounts of exchangeable cations as accurately as possible the cation contents of the a- and b-fractions

TABLE 14

Results from the extraction experiments

SOIL NUMBER	M.E. CATIONS PER 100 GRM. OF SOIL							
	Water extraction	Ammonium acetate extraction					Reduced total [(a + b) − (c + d)]	Reduced total minus water soluble
		a	b	c	d	Total		
1	2	3	4	5	6	7	8	9
7A	0.249	2.538	0.137	0.117	0.137	2.929	2.421	2.172
49A	0.117	3.318	0.193	0.097	0.077	3.681	3.337	3.220
50A	0.225	4.490	0.176	0.117	0.137	4.920	4.412	4.157
14A	0.176	16.836	1.562	0.390	0.195	18.983	17.813	17.637
48A	0.215	7.320	0.117	0.078	0.098	7.613	7.261	7.046
79A	0.156	24.298	3.074	1.171	0.683	29.226	25.518	25.362

are added and then corrections for solubility are made by subtracting the amounts of cations in the c- and d- fractions (column 8), and finally the cations from water-soluble salts are subtracted (column 9). The numbers in column 9 should consequently be the amounts of exchangeable cations.

Comparisons between the amounts of "exchangeable cations" found by electrodialysis (I) and by ammonium acetate extraction (II) give the following results:

	I (Table 13)	II (Table 14)
Soil 7A	2.188 M.e.	2.172 M.e.
Soil 49A	2.954 M.e.	3.220 M.e.
Soil 50A	4.001 M.e.	4.157 M.e.
Soil 14A	18.549 M.e.	17.637 M.e.

As may be seen, the agreement between the two methods is good for these soils when in both cases corrections are made for the solubility effect. The parabolic equation referred to previously, has also been applied to the soils

described, but in these cases it gives too small reductions of the total amounts of cations found if the ammonium acetate method is used as standard. The data presented by Odén and Wijkström (13) show, however, that the equation given by these authors seems to be a very good mathematical expression of the process of weathering caused by electrodialysis.

According to table 14, the amounts of exchangeable cations for soil 48A are 7.046 M.e., and for soil 79A, 25.362 M.e. From table 12 it may be seen that the total amounts of cations found for these soils in the electrodialysis experiments are greater than the sums mentioned. The surplus must be results of solubility effect during the experimentations, but, as previously stated, these experiments were not continued long enough to reach constant cation liberation such that corrections can be made.

It is of interest to call attention to the great difference in the amounts of exchangeable cations which are found for the two types of soils used in this investigation. According to table 1, which shows the total amounts of the most important base cations in the soils, the Volusia silt loam soils should contain but little less of cations than the Ontario loam soils. In the content of exchangeable cations, however, the difference is great in favor of the Ontario loam soils. The Ontario loam is known as a very productive type of soil in comparison to the Volusia silt loam (9, p. 110) and one of the reasons why might be the greater content of easily available base cations.

Checking the results from the electrodialysis experiments as well as the ammonium acetate extractions performed gave very good agreement for experiments made under similar conditions. The previously mentioned verification of the determinations of the total amounts of cations from the extraction experiments as chlorides by electrodialysis of aliquots of the filtrate and titration of the bases in the cathode water gave practically the same results as the $AgNO_3$ titration.

SUMMARY

This paper presents results from a series of electrodialysis experiments performed in order to show the influence of various experimental conditions on the speed of cation liberation from certain soils. The conditions investigated are differences in the concentration of the soil suspension, differences in the distance between the electrodes, differences in voltage, and differences in membranes. The results are given in connection with the description of the various experiments.

Determinations of the total amounts of exchangeable cations in the investigated soils by extraction with ammonium acetate were also made. The results are compared with the results from the electrodialysis experiments and an attempt is made to distinguish between the total quantities of cations liberated from the soils and the amounts of exchangeable cations.

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PLATE 1

APPARATUS USED IN EXPERIMENTS

FIG. 1. The author's electrodialysis apparatus
FIG. 2. Mechanical dispersion and stirring equipments

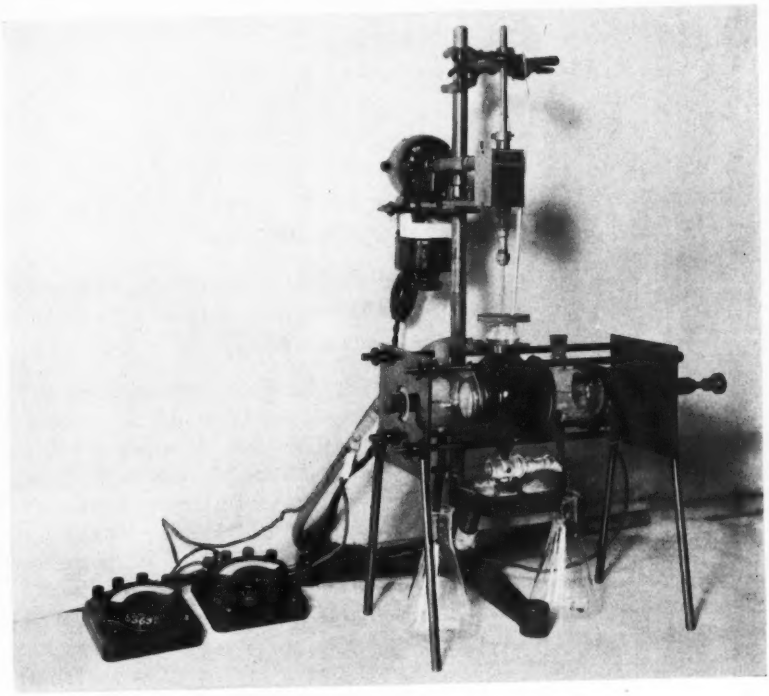

FIG. 1

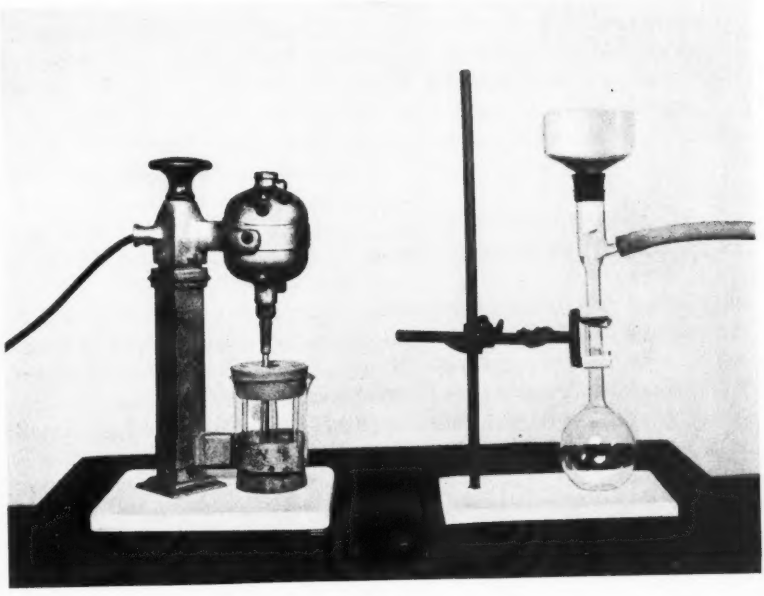

FIG. 2

THE DETERMINATION OF NITRATES IN SOILS CONTAINING SOLUBLE ORGANIC MATTER

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The determination of nitrates by the phenoldisulfonic acid method in humus materials, or in soils which contain soluble organic matter, is often made difficult or impossible by discoloration caused by the organic matter. This is especially true when the nitrate content of the material being studied is low. If the nitrate content of the material is fairly high, such as occurs in some muck soils after incubation, the discoloration may be disregarded if it is not too intense.

The writer, while studying forest soils in which the nitrate content is usually low, found that nearly all samples of litter and pronounced duffs yield water solutions which are too highly colored to determine even approximately the quantity of nitrate nitrogen present, using the ordinary methods of procedure. Such clarifying agents as aluminum and copper hydroxides, bone black, and G-elf carbon black mainly remove material in suspension. Soluble discoloring materials are not greatly affected by them.

A method suggested by Syme (2), which involves the oxidation of the soluble organic material by means of potassium permanganate, has proved ineffectual. This is mainly because of the difficulty in adding exactly the right amount of oxidizing reagent, the least excess of which discolors the solution still further. Also, after the permanganate has acted upon the organic matter a residue remains, which is difficult to filter off.

A simple and convenient method which has proved to be very satisfactory, giving clear and uncolored solutions in practically every instance, involves the use of concentrated hydrogen peroxide (superoxol) and ammonium hydroxide. The procedure is as follows:

A soil-water mixture is prepared in the usual manner, but without the addition of a precipitating agent. After the mixture is filtered a little powdered $Ca(OH)_2$ (0.5 gm. to 100 cc. solution) is added to the filtrate. If the hydroxide is added to the soil-water mixture before filtering, the discoloration is accentuated in many cases. The filtrate should be stirred after the addition of the hydroxide and allowed to stand for several minutes and then filtered. This procedure removes much, if not most, of the coloring matter from the solution. Often, however, some discoloration will remain.

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An aliquot of the filtrate is placed in a porcelain dish and evaporated to dryness. If any soluble organic matter is present the residue or incrustation in the bottom of the dish will be brownish in color, the intensity of which depends upon the nature and amount of the organic matter present. The evaporating dish is allowed to cool and approximately 0.5 cc. of 1:1 ammonium hydroxide is added. The dish is then rotated carefully in order to wet thoroughly all of the residue. Five to fifteen drops of superoxol are then added, according to the intensity of the brown color, and the dish is again rotated until the superoxol is in thorough contact with all of the residue. The reaction may be accelerated by placing the dish on a steam bath and carefully evaporating the solution to dryness. If any discoloration remains the residue should again be wetted with the ammonia and superoxol and

TABLE 1

Nitrates recovered from soils containing known amounts of nitrates

KNOWN AMOUNT OF NITRATES PRESENT	TOTAL NITRATES RECOVERED							
	Treated				Untreated			
	1	2	3	4	1	2	3	4
p.p.m.								
1	1	1	1	1−	1+	1	1	1
3	3	3	3−	3+	3	3	3+	3
5	5−	5	5	5	5	5+	5−	5
10	10	10+	10+	10+	10	10	10−	10
20	19	20	20	19	20	20	20	19
30	30	30	31	31	30	29	30	30
50	49	51	49	50	50	48	50	50
100	101	99	98	101	100	101	101	101
300	297	300	298	302	302	299	298	300
500	496	495	503	501	498	501	500	498
1,000	1,000	1,005	994	1,003	998	997	1,001	1,002

evaporated. If a discoloration should still persist, it is most probably due to traces of iron or manganese and not due to organic matter. Aluminum and silica may also be present. In either case further attention need not be given to the color because these substances will not interfere with the final reading operation when comparison with the standard color is made. The residue is finally wetted with ammonia and evaporated to dryness in order to expel any excess of the superoxol. From this point the regular procedure is followed.

Most of the discoloration due to soluble organic matter can also be removed by superoxol after the yellow nitrate color has been developed in the ordinary manner. This procedure is not as effective as the one outlined in the foregoing and requires the use of much more superoxol.

In order to determine whether any inaccuracy is caused by the use of

superoxol, i.e., whether nitrates are formed or destroyed, tests were made using known amounts of nitrates. Satisfactory checks were obtained in all instances, whether the nitrate content was high or low, as shown in table 1.

In the same manner it was found that nitrites present in the soil solution would not be oxidized to nitrates to any determinable extent. Nitrites are extremely unstable in the presence of strong ammonia and are almost immediately lost in the form of a gas or a mixture of gases. Nitrites are also unstable in the presence of strong acid and would be lost in a similar manner when phenoldisulfonic acid is added to the residue in the regular procedure. Gaarder and Hagem (1) in Norway, write that contrary to most investigators, they find that nitrites in soil solutions are oxidized to nitrates when treated with the phenoldisulfonic acid.

It was found, however, that when large amounts of nitrites were used—several hundred parts per million—a slight oxidation of nitrites to nitrates occurred because, a slight increase over the known amount of nitrates present was obtained. Since soils rarely contain more than traces of nitrites, it is believed that the method here outlined is very accurate and practicable for the determination of nitrates in soils which contain soluble organic matter.

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SOIL PROFILE STUDIES: IV. MORPHOLOGICAL AND CHEMICAL EVIDENCE OF PODZOLIZATION

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THE A_0 LAYER

The general morphological and chemical features of the A_0 layer in a typical podzol profile on a loamy parent material are as follows:

A_0 is the humus-decay accumulative layer which consists of leaf mould and forest litter, about 2 to 3 or more cm. thick, depending on conditions referred to in a previous publication (2). It corresponds to what the foresters refer to as the F and H layers. It is intermingled with some mineral soil material. This layer is accumulative in the sense that the organic matter of plant and animal origin upon decay leaves behind humus substances which are decomposition products and newly synthesized complexes of biological and chemical origin.

The carbon, oxygen, nitrogen, and hydrogen which make up the bulk of the organic matter originate in the atmosphere and hydrosphere. And it is through the organic matter that the atmosphere and hydrosphere react with the aid of the biosphere agency on the lithosphere in the process of soil formation.

That portion of the completely decomposed—in other words, mineralized—organic matter from the humus accumulative layer leaves behind mineral substances. These minerals originally come from the lower horizons through the agency of growth and in that way A_0 is genetically related to the entire body of the soil profile.

Mineralization process

A portion of the minerals combines with the humus substances, forming the organic complexes such as Ca, Mg, Mn, Fe, and Al humates. Because of the carbonic acid formed in the process of decomposition, the nitric acid—in the nitrification process, sulfuric acid—in the oxidation of sulfur compounds, and the organic acid as split products in the process of organic matter decomposition, some of the bases in the humate complexes are replaced by hydrogen and the material of the A_0 is therefore almost always acid. Some of the hydrogen saturated complexes become mobile because of their high dispersion

[1] Journal series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

and they move downward. With them move the other portion of the minerals and the free acids. They react with the mineral constituents of the underlying horizon, decompose the silicates, and release the bases which join the substances from the A_0 in a further downward movement.

Thus A_0 is the starting point of many reactions. It is the potential source and storehouse of the substances which react with the underlying horizons and impart to the profile the characteristic features of podzols.

Base-exchange capacity

One of the distinctive chemical properties of A_0 is its high base-exchange capacity, especially when compared with the same property in the other horizons. In no zonal soil type is the difference in base exchange capacity between the A_0 and the underlying horizons so great as in the podzol zone.

TABLE 1

*Some chemical properties of the A_0 layer**

SOIL SERIES	DEPTH OF A_0	REACTION		BASE EXCHANGE CAPACITY	UNSATURATION		BASE EXCHANGE CAPACITY OF HORIZON C
		H_2O extract	Neutral salt extract				
	cm.	*pH*	*pH*	*m.e.*†	*m.e. of H*	*per cent*	*m.e.*
Sassafras loam	3	5.0	3.8	22.3	19.7	88.3	5.2
Penn silt loam	3	5.2	4.3	26.4	18.64	70.6	11.2
Chester gravelly loam	3	6.2	5.0	18.5	5.83	31.5	5.3
Washington loam	5	7.2	6.8	37.2	1.98	5.3	5.03

* The soils on which the analyses are presented are not true podzols. They are members of the podzol zone, the southern belt variety, which was discussed in an earlier publication (2).

† M.e. is the milligram equivalents per 100 gm. of soil. The Ba-acetate method was used in determining the base-exchange capacity and the unsaturation.

Another distinctive chemical property of A_0 in the podzols is its high unsaturation.

In table 1 a few properties of A_0 in a number of soils in New Jersey are presented.

The data in table 1 show that the base-exchange capacity of A_0 is fairly high. For comparison the exchange capacity of the parent material (horizon C) is given. The latter is taken as a measure of the base-exchange capacity of the mineral portion of the soil. As a matter of fact, it is difficult to determine the constant for the base-exchange value of the mineral fraction which should be applicable to all the profile horizons, even in any one particular soil. It is variable because of the dynamic nature of the soil forming processes. For purposes of orientation the exchange capacity value of C might be used as the starting point to bring out the facts about the comparative rôle of the organic and mineral fractions in the base exchange reactions of the soil. The

figures in table 1 reveal that the seat of the base-exchange capacity in A_0 lies primarily in the organic fraction.

Mattson (3) prepared by the Odén method a sample of "humic acid" which he found to have an exchange capacity of 306.4 m. e. per 100 gm. This would seem to indicate that the organic matter of the A_0 layer does not contain much of this humic acid. Analyses of 12 A_0 samples (only 4 are given in table 1) have given only one case where the base exchange capacity was equal to 37.2 m.e. per 100 gm. Thus, at best, the organic matter would contain about 10 per cent of the "humic acid." We know, however, that the humic acid is not the only organic constituent capable of base exchange. It may, therefore, be inferred that the state of decomposition which is responsible for the formation of the many organic complexes in A_0 will influence the base-exchange capacity. In table 2, reproduced from Muller (5), figures are presented which show that the stage of decomposition does influence the base-exchange capacity of organic materials.

TABLE 2

Base exchange in decomposing organic materials

TIME	BASE EXCHANGE PER GRAM DRY WEIGHT		
	Soybeans	Straw	Manure
	m.e.	*m.e.*	*m e.*
Beginning	0.58	0.00	0.73
After 3 weeks	....	0.22	1.03
After 2 months	0.52	0.30	1.09
After 3.5 months	0.48	0.33	1.11
After 6 months	1.20	0.38	1.45
After 9 months	....	0.59	1.67

Unsaturation of A_0

Table 1 also brings out the next important chemical property of the A_0 layer in podzols, its unsaturation. It varies from 5.3 to 90 per cent. This wide variation is due primarily to two factors: parent material and vegetation.

Parent material as a factor of unsaturation

In the podzol process of soil formation the mineralized bases from the A_0 layer go downward to be partially "filtered" out, or adsorbed, by the B horizon. There they are caught by the plant roots and, together with the bases which are picked up by other roots in the soil solution of the intermediate layers—between A_0 and B—, they are transferred to the tops of the plant cover. They appear again at the surface when the leaves, twigs, and branches die and are redeposited in the A_0 layer to be mineralized. The richer the parent material the greater the circulation of the bases; the state of unsaturation will therefore depend on the balance between the outgo and return of the bases.

Because of that, soils which have a parent material rich in bases will resist podzolization. This seems to be the case with the Washington loam as shown in table 1. Its parent material consists of glacial drift which contains some limestone. Naturally more calcium is pumped up from the lower horizons and redistributed in A_0. This is reflected in the reaction of the material. A water extract of it shows a pH of 7.2 and even a neutral salt extract shows only slight acidity—pH 6.8.

Ammonification and unsaturation

This type of unsaturation is not to be confused with a temporary condition of a similar nature—increase in alkalinity—because of the formation of ammonia in the process of ammonification. It is well known that the base exchange complex of the podzols, especially the A_0 layer, may contain some ammonia. The little work done by the author indicates that it varies seasonally and in the late spring ammonia may be detected frequently. Undoubtedly it is linked up with the relative supply of carbohydrates and nitrogenous substances. This problem needs to be investigated further.

Vegetation as a factor of unsaturation

The wide variations in the ash content of plants contribute a good deal to the speed of podzolization. Unfortunately not very many analyses on the forest litter are available. It is known, however, that as a rule the hardwoods contain a higher ash content than the conifers.

In table 3 ash analyses and CaO content of wood, bark, and forest litter of a number of hardwoods and conifers are given.

A comparison of the average ash content of the forest litter in the conifers[2] with the average ash content of the litter in hardwood shows that the hardwoods bring into circulation more ash than the conifers. *The average ash content of the conifers is equal to 2.54 per cent* with a minimum of 1.29 and a maximum of 3.31 per cent, whereas *the average of the hardwoods is equal to 6.63 per cent* with a minimum of 3.85 per cent and a maximum of 11.74 per cent. There is 2.6 times as much ash furnished by the hardwood litter as by the conifer litter. Even the wood and bark of the hardwoods has a higher ash content than the wood or bark of the conifers, as shown in table 3.

Another point to be considered in this connection is the rate of decomposition of the litter. Hardwood litter decomposes much faster and more completely than conifer litter. There are fewer intermediary split products of decomposition under conditions of hardwood litter than under conifer litter. Thus the final products of mineralization are more active in the hardwood

[2] The average for the conifers was obtained by adding the ash percentages from No. 1 to 10 in table 3 and dividing by 8, the number for which analyses are shown. Similarly the average ash content of the hardwoods was calculated.

TABLE 3

Ash constituents of some forest trees

NUMBER	SPECIES	ASH CONTENT IN			CaO CONTENT IN	
		Wood	Bark	Forest litter (old leaves)	Forest litter	Wood
		per cent	*per cent*	*per cent*	*per cent*	*per cent*
1	Yellow pine (*Pinus mitus*)†	0.3765	.....	.....	....	0.163
2	Old field pine (*Pinus mitus*)†	0.2620	1.81	.....	....	0.113
3	Red pine (*Pinus resinosa*)‖	.....	.....	2.30	....	.....
4	White pine (*Pinus strobus*)‖	.....	.....	2.70	....	.....
5	White pine (*Pinus strobus*)**	.....	.....	2.90*	....	.....
6	Pine (*Pinus sylvestris*)§	.....	.....	1.46	0.59	.....
7	Pitch pine (*Pinus rigida*)**	.....	.....	1.29	....	.....
8	Black pine (*Picea nigra*)†	0.2874	.....	.....	....	0.123
9	Red spruce (*Picea rubra*)‖	.....	.....	3.30	....	.....
10	Red spruce (*Picea rubra*)**	.....	.....	3.31	....	.....
11	Balsam fir (*Abies balsamea*)**	.....	.....	3.08	....	.....
12	Larch (*Larix europaea*)**	.....	.....	6.09	....	.....
13	Red maple (*Acer rubrum*)‖	0.2714†	3.48†	4.40	....	.....
14	Red maple (*Acer rubrum*)**	.....	.....	4.08	....	.....
15	Sugar maple (*Acer saccharum*)‖	.....	.....	11.30	....	.....
16	Sugar Maple (*Acer saccharum*)**	.....	.....	6.68	....	.....
17	Black locust‡	.....	.....	11.74	....	.....
18	Birch‡	.....	.....	4.68	....	.....
19	Grey birch (*Betula populifolia*)‖	.....	.....	4.10	....	.....
20	Grey birch (*Betula populifolia*)**	.....	.....	4.07	....	.....
21	Beech (*Fagus grandifolia*)**	.....	.....	4.49	....	.....
22	Beech (*Fagus grandifolia*)**	.....	.....	9.26	....	.....
23	Beech (*Fagus grandifolia*)**	.....	.....	9.36	....	.....
24	Beech (*Fagus grandifolia*)**	.....	.....	7.11	....	.....
25	Beech (*Fagus grandifolia*)§	.....	.....	5.57	2.46	.....
26	Bird cherry‡	.....	.....	7.24	....	.....
27	Chestnut (*Castanea vulgaris*)†	0.1500	3.43	4.55‡	....	0.050
28	Hickory (*Carya tomentosa*)†	0.6468	3.86	.....	....	0.161
29	Redoak (*Quercus rubrum*)†	0.7687	6.28	.....	....	0.246
30	White oak (*Quercus alba*)†	0.3927	5.88	.....	....	0.083
31	Post oak (*Quercus obtusiloba*)†	0.9224	11.80	.....	....	0.301
32	Dogwood (*Cornus Florida*)†	0.8029	9.62	.....	....	0.223
33	Ash (*Fraxinus americana*)†	0.4247	.....	10.26**	....	0.075
34	Poplar (*Populus grandidentata*)**	.....	.....	3.85	....	.....
35	Sycamore (*Plantanus occidentalis*)†	1.00	.....	.....	....	.....

* Average of three lots.
† Results taken from White (9).
‡ Results taken from Tollens (7).
§ Results taken from Glinka (1).
‖ Results taken from C. W. Watson, personal communication from unpublished data.
** Results taken from Melin (4).

forests, and, being basic in reaction, they contribute a great deal to the retardation of the podzolization process in hardwood forests. All in all, the hardwood vegetation, furnishing a higher ash and consequently higher base content, will help to keep the unsaturation of A_0 at a low level. This in turn will retard the process of podzolization.

The case of the brown soils ("Braunerde" of Ramann) which are climatogenically in the podzol zone and still not thoroughly podzolized has been discussed elsewhere (2). It is the parent material and the vegetation that enter into the picture of the process of forming the "Braunerde."

THE A_1 HORIZON

Morphological[3] *and chemical characteristics*

In a true podzol the A_1 horizon is the mineral horizon lying immediately below the A_0 layer. On a loamy parent material its general morphological features are as follows: It is light gray with a straw-colored tinge, impregnated with some humus material, and is of a powdery, loose, silty structure, with a sandy appearance and fine porosity. As a matter of fact it has no structure and this structureless condition is one of the distinctive characteristics of this horizon. The texture is not sandy either, rather it is loamy. In thickness it varies, but on the average it is about 14 cm.

Chemically A_1 is distinguished by its low base exchange capacity—as compared with A_0—loss of bases and sesquioxides, enrichment in SiO_2, and a comparatively high unsaturation.

In a medium podzolized soil where the morphological attributes are not in evidence the chemical properties determine the degree of podzolization.

A morphological study made on the profiles of the loam soils mentioned in table 1 reveals no apparent features of a podzol. The A_1 horizon instead of being light gray is yellowish brown in the Sassafras loam; reddish brown to brown in the Washington loam; darker reddish brown in the chestnut, which contains a considerable amount of organic matter; and brownish red in the Penn silt loam.[4] Thus the A_1 horizons in the soils mentioned do not exhibit the morphological features which correspond to those in a true podzol loam.

When we come to examine the chemical properties of the A_1 horizons in the respective soils as presented in table 4, we note that these do correspond, or at least show tendencies to correspond to the chemical attributes of the loam podzols.

[3] There are some physical properties of the soil, such as structure, and porosity, which are easily detected by morphological methods and are therefore considered together with the morphological characteristics of the soil.

[4] The Penn series of soils seem to belong to what Glinka (1) calls "endodynamomorphic soils in which the factor of the parent material predominates over the climatic factor for a long time in the process of soil formation."

Base exchange capacity and unsaturation

In table 5 a comparison is made on the base exchange capacity and unsaturation of the A_0, A_1, and C horizons.

TABLE 4

Total chemical analyses of soil profiles

LABORATORY NUMBER	HORIZON	DEPTH OF HORIZON	REACTION		SiO_2	Fe_2O_3	Al_2O_3	P_2O_5	CaO	MgO	MnO_4	BASE EXCHANGE CAPACITY	UNSATURATION (H)	
			H_2O extract	Neutral salt extract										
		cm.	*pH*	*pH*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*m.e.*	*m.e.*	*per cent*
						Sassafras loam								
1	A_0	3–4	5.0	3.8	76.05	3.127	5.322	0.123	0.347	0.472	.....	22.30	19.70	88.3
2	A_1	15	5.2	4.4	85.33	4.128	5.086	0.080	0.247	0.479	0.144	5.46	5.14	94.1
3	A_2	18	5.0	4.4	85.78	4.575	8.562	0.085	0.456	0.611	0.312	4.74	4.27	93.6
4	B	14	5.1	4.4	84.35	4.575	6.23	0.101	0.513	0.629	0.225	4.98	4.05	81.3
5	C	..	4.9	4.5	84.30	4.743	6.75	0.090	0.339	0.679	0.157	5.2	4.05	78.0
						Penn silt loam								
7	A_0	3–4	5.2	4.3	52.55	6.08	17.06	0.131	0.744	1.729	0.445	26.4	18.64	70.6
8	A_1	12	4.9	4.5	57.85	8.15	18.09	0.071	0.304	1.743	0.487	14.1	7.56	53.6
9	A_2	26	4.8	4.5	56.7	8.53	19.53	0.056	0.342	1.993	0.238	10.7	7.56	70.6
10	B	38	4.9	4.3	54.97	9.54	20.36	0.0467	0.206	2.166	0.425	11.4	7.56	66.3
11	C	..	5.1	4.3	55.10	9.21	20.20	0.055	0.206	2.053	0.437	11.2	7.64	68.2
						Chester gravelly loam								
22	A_0	3–4	6.2	5.0	63.20	5.44	10.905	0.127	0.831	0.604	0.200	18.5	5.83	31.5
23	A_1	12	5.5	4.4	71.45	6.418	10.717	0.092	0.693	0.669	0.281	7.19	4.568	63.5
24	A_2	16	5.4	4.4	72.55	7.142	9.877	0.097	0.736	0.773	0.275	6.31	3.46	54.8
25	B_1	15	5.2	4.4	68.37	9.290	10.565	0.102	0.583	0.769	0.344	6.8	4.49	66.0
26	B_2	43	5.2	4.4	63.25	14.575	11.253	0.108	0.363	0.263	0.294	6.61	3.34	50.5
27	C	..	5.4	4.6	68.92	7.54	11.002	0.066	0.565	0.301	0.338	5.3	2.38	45.0
						Washington loam								
17	A_0	3–5	7.2	6.8	61.40	5.86	10.115	0.175	1.063	0.778	0.325	37.20	1.98	5.3
18	A_1	21	5.3	4.4	71.57	6.64	11.297	0.114	0.355	0.654	0.255	12.00	5.97	50.0
19	A_2	11	5.1	4.4	69.12	7.73	12.74	0.131	0.286	0.636	0.275	8.16	5.37	65.8
20	B	19	5.3	4.4	65.55	8.43	13.52	0.132	0.215	0.579	0.275	6.24	3.19	51.1
21	C	..	5.4	4.8	66.3	8.567	12.93	0.128	0.237	0.692	0.183	5.03	2.2	43.7

It is striking what a drop in base exchange capacity takes place from A_0 to A_1. Undoubtedly this drop may be explained by the difference in the organic matter content of A_0 and A_1. With the tremendous base exchange

capacity inherent in the humus complexes, it may be inferred that the mineral horizon A_1 with its low base exchange capacity is poor in organic matter. If we examine the data in table 5 a little closer, we see that the base exchange capacity of A_1 in the Sassafras soil corresponds to that of C, the parent material, which is supposed to contain only traces of organic matter. Looking at it from this angle, one would be apt to surmise that in the Sassafras soil the base exchange capacity of A_1 is due to the mineral complexes. But we must not forget that A_1 is the horizon of eluviation where the leaching processes are instrumental in decomposing the mineral complexes, in breaking up the kaolin nuclei, leaving behind SiO_2. All of that contributes to a decrease

TABLE 5

Base exchange and acidity in A_0, A_1, and C

SOIL SERIES AND HORIZONS	REACTIONS		BASE EXCHANGE CAPACITY	H	UNSATURATION
	H_2O extract	Neutral salt extract			
	pH	*pH*	*m.e.*	*m.e.*	*per cent*
Sassafras loam A_0	5.0	3.8	22.3	19.7	88.30
Sassafras loam A_1	5.2	4.4	5.46	5.14	94.10
Sassafras loam C	4.9	4.5	5.20	4.05	78.00
Penn slit loam A_0	5.2	4.3	26.40	18.64	70.60
Penn slit loam A_1	4.9	4.5	14.10	7.56	53.60
Penn slit loam C	5.1	4.3	11.20	7.60	68.20
Chester gravelly loam A_0	6.2	5.0	18.50	5.83	31.50
Chester gravelly loam A_1	5.5	4.4	7.13	4.57	64.00
Chester gravelly loam C	5.4	4.6	5.30	2.38	45.00
Washington loam A_0	7.2	6.8	37.20	1.98	5.30
Washington loam A_1	5.3	4.4	12.00	5.97	50.00
Washington loam C	5.4	4.8	5.03	2.20	43.70

of the base exchange capacity of the mineral fraction especially in an acid medium as the case is with the A_1, which is brought out by the pH values. It must therefore be concluded that some of the base exchange capacity in A_1 is to be attributed to organic matter.

An examination of the data in table 5 on the other soil series shows that A_1 has a greater base exchange capacity than C. In the Washington loam it is almost 2.5 times as high. This indicates a high organic matter content. Thus a comparison of the base exchange capacity of A_1 (for that matter any other horizon) and C may serve as an index of the organic matter content of the respective horizons. This problem is under investigation and in due time the results will be reported.

The high unsaturation of A_1 in the four series reported in table 5 is ample

chemical evidence of the podzolized state of these soils. In all soils, except the Penn series, the percentage of unsaturation of A_1 is higher than that of A_0 and C. The Penn series of soils does not behave as a climatogenic[5] soil: its characteristic features were formed not so much because of the climate and vegetation factors but because of the specific nature of the parent material. According to Zakharov (11) such a soil is to be called "lithogenic" instead of "climatogenic." And even in this soil one may find chemical evidence of podzoliation, as will be pointed out presently.

Silica

Coming back to table 4, which gives the inorganic constituents of the soils under discussion, we may note that in all cases the SiO_2 is higher in A_1 than in any other horizon except A_2. In a true podzol the difference in SiO_2 content of A_1 and A_2 is more marked than in podzolized soils—those discussed in this paper.

The fundamental reactions involved in enriching the A_1 horizon with SiO_2 in the podzol process of soil formation are as follows: The A_1 horizon is subjected to the action of the carbonic acid formed by the respiration of roots and metabolic activities of microorganisms in decomposing organic materials, nitric acid from the processes of nitrification, sulfuric acid from the processes of oxidation of sulfur compounds, other inorganic acids like phosphoric and silicic in various forms, and finally the organic acids from the decomposition of organic matter. All of these acids which form both in the A_0 layer overlying the A_1 horizon and in A_1 itself react with the minerals, decompose them, set free first of all the alkali and alkaline earth bases, then split the kaolin nuclei, setting free the sesquioxides and leaving behind the SiO_2.

Calcium and magnesium

A low content of alkaline earth bases in A_1 in a soil with a relatively higher content of these in C is indicative of strong podzolization. These two bases, especially the Ca, circulate through the soil profile more than any of the other cations. They return in appreciable quantities to the A_0 through the medium of the roots and plant residues which are deposited at the surface as outlined previously. The data in table 4 on the Ca and Mg content of A_0 show clearly that it is the organic matter which mobilizes the bases.

In the soils under consideration the Ca and Mg content is relatively high, even higher than in the C horizon—the parent material. From the data available on the chemical composition of loamy podzols it is known that the Ca and Mg content is rarely higher in the A_1 horizon than in the C. These soils are therefore not true podzols since they show consistently high Ca and Mg in A_1 and even in A_2. It is well to remember that in true loamy podzols the Ca and Mg is frequently higher in A_1 than in A_2 just because of the higher organic matter content in this horizon.

[5] More about the climatogenic soils is to be found in a previous publication (2).

Iron and aluminum

None of the chemical constituents of the soil material in the profile of the podzols are more indicative of the state of podzolization than the sesquioxides. In the circulation of the elements through the profile, the sesquioxides are among those which do not return in any appreciable quantities as the bases do. They are always lower in the A_1 horizon than in the parent material. And the greater the difference between A_1 (and more so in A_2, as we shall see) and C, the greater is the degree of podzolization.

In the podzol zone the conditions inducive to the movement of the sesquioxides are a high hydrogen-ion concentration, depletion of electrolytes, especially bases and anions with which the sesquioxides combine, or in other words, the conditions which keep the sesquioxides below the isoelectric point of precipitation. These conditions prevail in A, the horizon of eluviation, and A_1 as a component of A reflects these conditions by becoming impoverished of the sesquioxides. This is true for podzols with a mature profile. In the soils under consideration, as shown in table 4, the sesquioxides in A_1 are lower than in C, a true indication of the podzolized condition of these soils, but the difference between the two horizons is not great enough to place these soils in the strongly podzolized class.

An important characteristic of the A_1 horizon is its power to fix humates with the alkaline earth bases and sesquioxides which originate in the A_0 layer in the process of decomposition and mineralization of the organic matter. There is no accumulation of these in A_1 since they are also subject to decomposition. But in the circulation of the soil constituents these newly formed substances are temporarily retained in the A_1 horizon. The free acids and acid salts that pass beyond A_1 react with the mineral constituents of the underlying horizon which, because of that, is leached more than the overlying A_1 horizon.

THE A_2 HORIZON

Morphological and chemical characteristics

In a podzol soil of a loamy texture the A_2 horizon is a component part of the horizon of eluviation. It differs from the overlying A_1 horizon in being more thoroughly podzolized. Its morphological features are: The color is bleached ash-gray to whitish gray changing to a brownish tinge at the bottom. The average thickness of this horizon in a loamy soil is 14 to 16 cm. Structurally this horizon varies little from the horizon above, being loose and powdery when dry, smeary when wet, with little pore space, blending into a platy structure at the junction with the underlying horizon, sometimes with granules of ortstein or concretions.

None of the morphological features of the A_2 horizon are more pronounced than the bleached ash-gray color. It is this striking color that makes horizon A_2 the outstanding characteristic horizon in the podzol profile. As to the

source of the color there seems to be a general agreement that it is due to the SiO_2 which separates out from the decomposed kaolin and coats the soil particles. This process, as pointed out in the discussion on the SiO_2 content in the A_1 horizon, is intimately connected with the activity of the reaction products of the A_0 layer. But in A_1 the color is less pronounced because the humus complexes, being dark in color, obscure the color effects of the white SiO_2. In the A_2 horizon the prevailing organic matter complexes belong to the colorless "crenic" acid type as pointed out by Williams (10).

Chemically A_2 may be looked upon as an accentuated condition of A_1. It is lower in base exchange capacity than A_1, more unsaturated, usually lower in Ca and sesquioxides and higher in SiO_2. In a true podzol loamy soil the SiO_2 penetrates in tongue-like fashion into the underlying horizon B as shown in plate 1 reproduced from Zakharov (11).

As in A_1 there is no evidence of the characteristic morphological features of a podzol in the A_2 horizon of the soils investigated. It is true that the A_2 is slightly lighter in color than A_1, but it is due not to the SiO_2 coating, but to the lower humus content.

An analysis of the chemical data on the constituents of A_2 as given in table 4 shows that in some respects this horizon exhibits the chemical properties of podzolized soils.

Base exchange capacity and unsaturation

A graphic illustration of the tendencies of the base exchange capacity of the soils investigated as compared with that of a true podzol on a heavy loam as reported by Rodé (6) is given in figure 1. It will be noted that the base exchange capacity of this horizon is lower than that of A_1, which is in agreement with the general chemical features of a podzol. The tendency of the curves of the soils investigated is to follow the curve of the true podzol up to A_2. After that the curves depart from the tendency of the curve of the true podzol. This shows that the soils are podzolized to some degree, but that they are not true podzols.

The percentage of unsaturation of A_2 in two of the soil series—Chester and Washington—runs true to form as in podzols, that is, it is higher in this horizon than in any other. It is also high in the Sassafras series, but not higher than A_1, but higher than in any of the other horizons. In the Penn series the same tendency may be noted, even though it is not a true climatogenic soil. Thus the unsaturation of A_2 furnishes chemical evidence of the podzolized state of the soils investigated.

At this point it is worthy of note that the pH of the water extract of the soil material from A_2 is as a rule lower than in any other horizon. The highly unsaturated condition of this horizon is suggestive in this connection. The total acidity as measured by the milligram equivalents of hydrogen is low in A_2 when compared with the other horizons. This indicates a low buffer capacity.

SiO_2

The figures in table 4 show that in comparison with the C horizon there is an accumulation of silica in the A_2 horizon. In the Chester and Sassafras series the SiO_2 content is higher than in any other horizon. This property is true for genuine podzols, except that it is more sharply defined, i.e. the difference between the SiO_2 content of the A_2 and any other horizon is greater than in the soils under consideration.

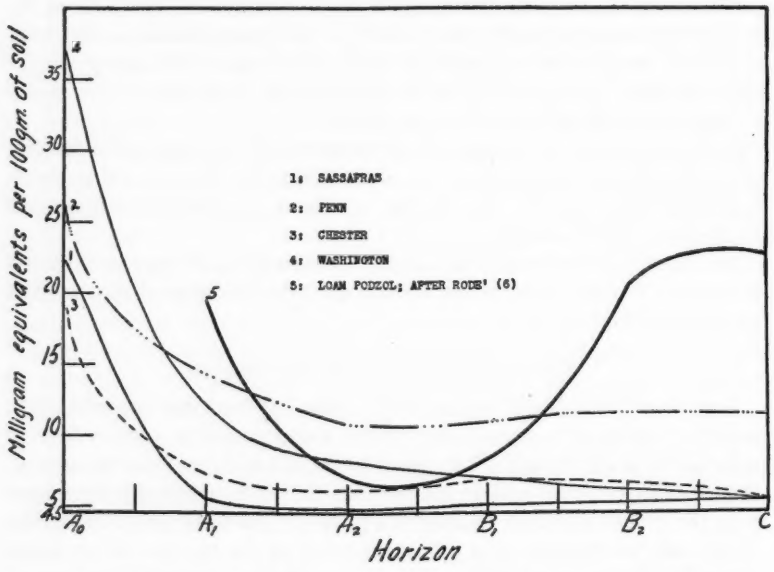

FIG. 1. BASE EXCHANGE CAPACITY OF SASSAFRAS, PENN, CHESTER, AND WASHINGTON SOILS, AND OF A LOAM PODZOL

Calcium and magnesium

What has been said about the bases Ca and Mg in connection with the description of A_1 holds true also for A_2. As long as A_2 is not completely podzolized—and hence leached—the base content will depend on the amount supplied by the A_0 horizon. From the data in table 4 it is clear that the Ca and Mg are high in A_2 (even higher than in A_1, except in the Washington series), a property contrary to the podzolized state of A_2 in a true podzol. It is an indication of the weakly podzolized condition of the soils investigated.

Iron and aluminum

The data in table 4 on the sesquioxide content of A_2 do not bring out clearly the fact that these soils are podzolized. Instead of being lower than in A_1

the sesquioxides are higher. And yet they are lower than in C—the parent material. From what has been said about the circulation of the sesquioxides in the soil profile (see section: "The A_1 horizon," iron and aluminum), the comparative values for A_2 and C do indicate a certain degree of podzolization.

THE B HORIZON

Morphological and chemical characteristics

The distinctive feature of the B horizon is that it is accumulative in character. It is known as the horizon of illuvation (washing in) in contrast to the A horizon known as the horizon of eluviation (washing out). The soil constituents which leach out from A are partly retained by the B horizon. This horizon is also enriched with the fine particles—mineral and organic—from the overlying A horizon by mechanical movement. It seems as if the B horizon were destined by the natural forces of soil formation to protect the soil body from being destroyed. By virtue of its accumulative properties this horizon becomes the storehouse from which the plant roots extract mineral nutrients and send them to the stems and leaves, which furnish the material for the A_0 layer—the starting point of the circulatory system of minerals and other substances in the process of soil formation. All of these facts leave a definite impression on the morphological, physical, and chemical features of this horizon.

In a loam podzol the accumulative horizon is divided into two subhorizons: B_1 and B_2 which are recognized as independent horizons because of variations in their morphological, physical, and chemical properties.

In plate 1 the B_1 and B_2 horizons are distinctly featured.

B_1 is usually 30–40 cm. deep, of a dull brownish coloration with some light and some dark streaks or veins, pocket-like on top and extending deeper in tongue-shaped fashion. The light colored markings are due to the accumulation of some of the podzolized material which moved into this horizon from the overlying A_2 horizon. The dark streaks represent the humus materials from A_0 and A_1 which pass in the sol state through A_2 and precipitate with the sols of iron, aluminum, and manganese by virtue of the higher concentration of electrolytes in this horizon and probably also as a result of the mutual coagulation effects of the oppositely charged colloids. (The SiO_2 and humus are negatively charged, whereas the iron and aluminum are, at the reaction existing in this horizon, positively charged.)

Because of the infiltration of materials from above, the B horizon is compact and heavy. It attains a more loamy texture, becomes sticky, and at the top begins to show signs of laminated or platy structure. With depth this structure becomes more apparent and toward the bottom this horizon exhibits a nutty and prismatic structure.

B_2 begins just below the prismatic structure and extends to a depth of about 30 to 40 cm. As a part of the accumulative horizon B_2 has properties similar to B_1, but it is poorer in organic matter and perhaps for that reason it is of a lighter

brownish coloration. It has fewer if any veins of the bleached material from A_2. At the bottom this horizon becomes lighter in texture, is not so compact and blends in with horizon C, the parent material.

It is to be noted that both B_1 and B_2 have the coatings of SiO_2, humus, manganese, and sesquioxides on the faces of the structural units, along the root paths and cracks. Infrequently, especially in lighter soils, orterde, ortstein, and concretions form along these cracks.

Chemically the B horizon is distinguished by the lower (when compared with the other horizons) SiO_2 content, high sesquioxide content, increase in bases and in capacity for base-exchange, and lower unsaturation (when compared with A_2). B_1, as a rule, has a higher organic matter content than A_2.

In the data in table 4, one might find, on the one hand, enough evidence of genuine podzol properties in the soils investigated and, on the other hand, chemical characteristics which show no, or only slight, podzolization. From the standpoint of morphological attributes one may note that only in one case—the Chester series—was it possible to differentiate two horizons (B_1 and B_2) in the horizon of accumulation, which indicates an immature profile; hence these soils are not true podzols.

Base exchange capacity and unsaturation

In the soils investigated the base exchange capacity of the B horizon has increased as compared with A_2, showing that some of the colloidal substances from the overlying horizons did move downward and stopped at the B horizon. It is to be remembered that the movement of the colloids, in which by the way, the base exchange capacity is high, is a true indication of the podzol zonal type of soil formation. The tendencies of the base exchange capacity are brought out with more clarity in figure 1. The base exchange capacity is high in A_0, decreasing in A_1 and continuing to decrease in A_2, and increasing again in B. The base exchange capacity of B is as a rule higher than that of C, except where that of the parent material is originally very high, as in the soil represented by curve 5, which has varved clay as the parent material.

True to form, the percentage of unsaturation in B is lower than that in any of the other horizons. This would indicate that the alkaline earth bases and probably potassium are present in the exchange complex.

SiO_2

Since very small quantities of the silicates are being attacked in the B horizon there is no free SiO_2 accumulating in it aside from the amorphous SiO_2 from the overlying horizons. Besides, it is enriched with iron, aluminum, and other colloidal complexes. All of that is inducive to a relative lowering of the total SiO_2. The data in table 4 on the SiO_2 content of the B horizon show this to be the case with the soils investigated.

Calcium and magnesium

In a true podzol the content of alkaline earth bases increases in the B horizon. As the humus sols move through the horizon of eluviation in an acid medium and reach the B horizon which is less acid, they precipitate and probably fix the alkaline earth bases and sesquioxides. It is known from the work of Mattson (3) that the colloidal humus complexes have a definite isoelectric point of precipitation which depends on the pH of the dispersion medium and on the presence of electrolytes. In podzol soils the conditions in the B horizon seem to be favorable—probably the proper pH and electrolyte content—for isoelectric precipitation of the humus sols with the bases and sesquioxides. That this condition has not been reached in the soils investigated may be judged from the data in table 4 on the Ca and Mg content of the B horizon. It is lower than in A_1 or even A_2, which shows that these soils are only in the early stages of podzolization. Whether they will ever become thoroughly podzolized is another question which needs further investigation. As it is, the alkaline earth bases in these soils seem to become tied up and fixed in the horizon of eluviation, as pointed out in the discussion on the A_1 horizon.

Iron and aluminum

It has been mentioned that the translocation and distribution of sesquioxides in the soil profile may serve as one of the best attributes of the state of podzolization of the soil. Very little of the iron and still less of the aluminum is returned to the A_0 horizon to go again into circulation through the soil body. As a result of that the sesquioxides accumulate in the B horizon and, even in the early stages of podzolization, an increase in these may be noted. They may be found in combination with the humus or as gels which infrequently are transformed into definite minerals such as gibbsite and limonite. They serve as cementing materials in the process of orterde or orstein formation. The work of Lundblad to which reference has been made (2) shows that in the B horizon of podzols there is a higher amount of gel than in any other horizon. This has also been proved earlier by Gemmerling, whose work has been quoted in an earlier paper (2).

From the data in table 4 on the sesquioxide content of the soils investigated, it is clear that we are dealing with distinctly podzolic soils, but the accumulation does not warrant their classification with the true podzols.

Phosphorus and manganese in the profile

No significant facts are brought out by the data on the Mn content of the various horizons. As a negative colloid Mn should undergo the reactions similar to humus, which is also negatively charged, provided both of them have the same isoelectric point of precipitation. It has been shown by Udulft (8) that these two colloids behave alike toward carbonates and bicarbonates.

Phosphorus is one of the very immobile anions in the soil, but in the podzols

there is usually an accumulation in the A_0 and B horizons. In the former it apparently exists in the organic forms whereas in the latter it is fixed by the

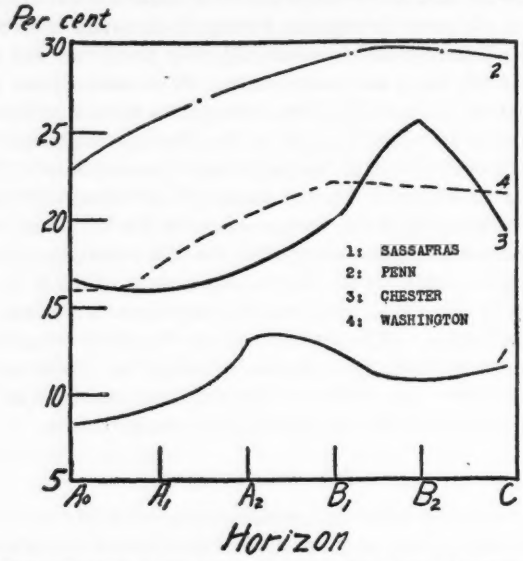

FIG. 2. SESQUIOXIDES OF SASSAFRAS, PENN, CHESTER, AND WASHINGTON SOILS

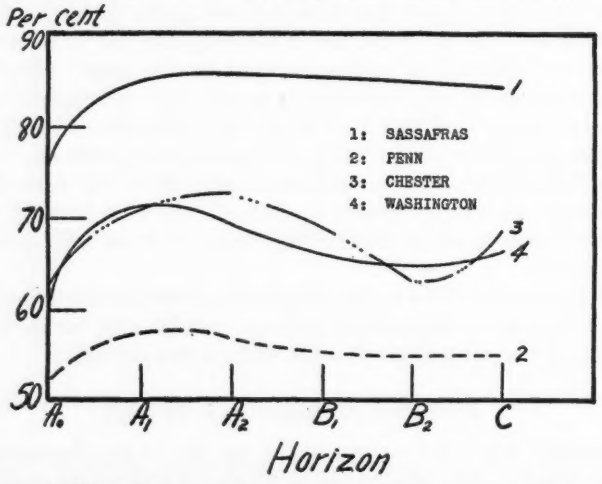

FIG. 3. SiO_2 OF SASSAFRAS, PENN, CHESTER, AND WASHINGTON SOILS

bases and sesquioxides. In the soils investigated it may be noted that the P_2O_5 content is invariably high in the A_0, but only indications of accumulation may be noted in the B horizon.

DISCUSSION

A survey of the chemical constituents in the profiles of the soils investigated clearly shows that the more typical reactions which occur in a podzol are to some degree apparent in these soils. Especially is this true for the values of base exchange capacity, sesquioxides, silica, and unsaturation.

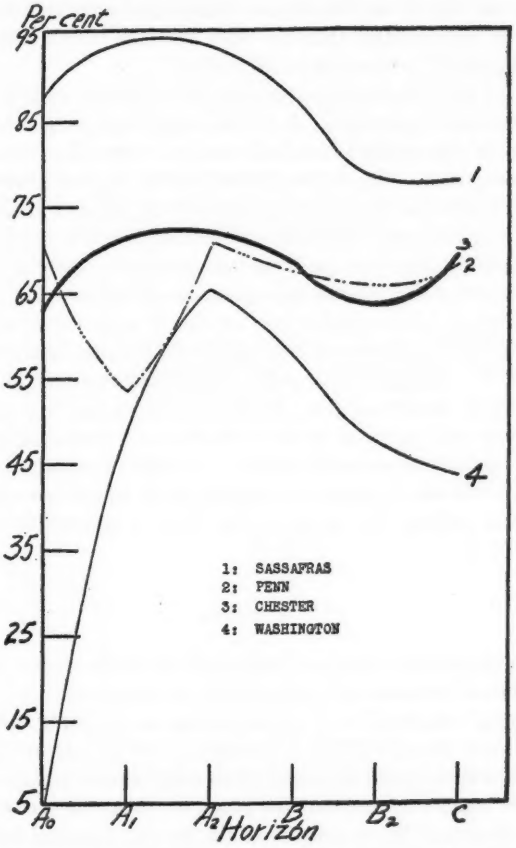

FIG. 4. UNSATURATION OF SASSAFRAS, PENN, CHESTER, AND WASHINGTON SOILS

In genuine podzols the base exchange capacity is high in the A_0, decreases abruptly in A_1, is still lower in A_2, and increases again in the B horizon. This is brought out in figure 1. The accumulation of the colloidal material in the B horizon is responsible for the increase in this property. Curves 1 to 4 show no sharp differences in the base exchange capacity of the horizons in the soils investigated, which is not true, however, for a genuine podzol as shown in curve 5.

This indicates that the soils investigated are weakly podzolized. The sesquioxides are low in the A_0, are not much lower and are sometimes even higher in A_1 and A_2, and are a good deal higher in B. Only in the Chester and Washington soils does this tendency seem to hold, as brought out in figure 2.

In figure 3 the distribution of the SiO_2 in the profiles of the soils is presented. True to form all soils show an increase in SiO_2 in the A_2 horizon and a decrease in the B horizon. Again the Chester and Washington soils indicate a state of higher degree of podzolization than the other two soils. And still there is no visible (morphological) evidence of podzolization.

In figure 4 the percentage of unsaturation in the various horizons of the soil profiles investigated is presented. It will be noted that the general tendency of the property of unsaturation is to be lower in A_0 than in A_1, increasing up to A_2, and decreasing in B. The degree of unsaturation depends primarily on the reserve of bases furnished by A_0 and on the amount of acids persisting in A_0. It is known that the organic acids—as intermediate products—produced in the decomposition of conifer litter are more resistant to complete decomposition (mineralization) than the intermediate products of hardwood or grass litter. One would therefore expect a higher unsaturation in conifer litter than in hardwood litter. These considerations may explain the peculiar behavior of curve 2 (the Penn series). This particular soil is endodynamomorphic in nature and therefore may not, because of that, follow in every detail the properties of a true climatogenic soil; but as far as the unsaturation is concerned, we need not fall back on its endodynamomorphic nature. It might be explained on the basis of the flora on this soil; it sustains a conifer stand (the other soils have the hardwoods) and perhaps the nature of the litter is responsible for the high unsaturation of A_0.

SUMMARY

The morphological and chemical features of the horizons in a typical loam podzol profile have been surveyed, illustrated, and presented.

A discussion of unsaturation as related to parent materials and vegetation with some data on the ash content of a number of species of forest trees brings out the facts about the speed of podzolization under various plant covers.

The soils for which chemical data are presented show evidence of podzolization; this is illustrated by an analysis of the various chemical indexes which serve as criteria for the degree of podzolization.

On the basis of the data in tables and figures a discussion is presented for each horizon individually, covering the properties of unsaturation, base exchange capacity, sesquioxide, SiO_2 and alkaline earth base content.

The distribution of P_2O_5 and manganese through the profile is also discussed on the basis of data presented.

From the data presented it is clear that the soils investigated are podzolized to a certain degree; they are what some like to call "podzolic soils."

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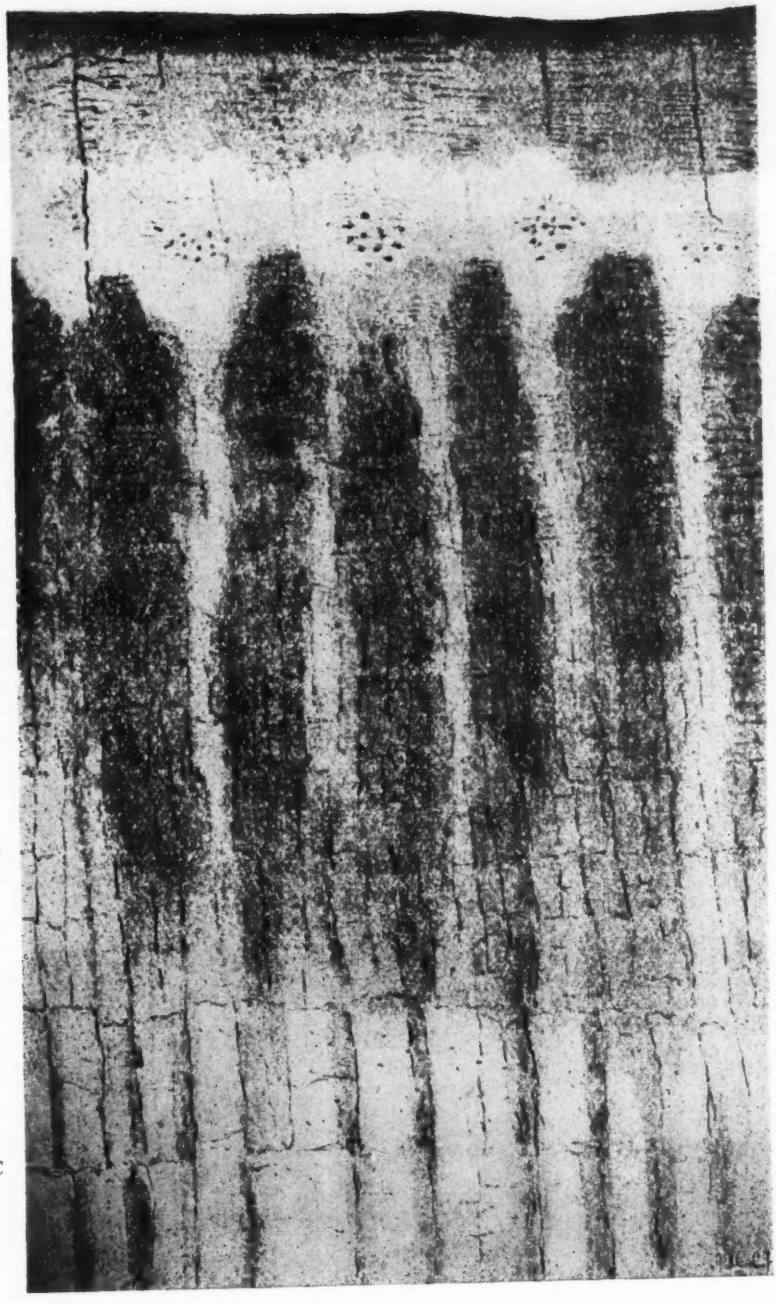
PLATE 1

A Typical Loam Podzol Profile

PLATE 1



BOOK REVIEW

Principles of Soil Microbiology, second edition, thoroughly revised. By SELMAN A. WAKSMAN, Professor of Soil Microbiology, Rutgers University, and Microbiologist of the New Jersey Agricultural Experiment Stations. The Williams & Wilkins Company, Baltimore, 1932. Pp. xxviii + 894, pl. 15, figs. 83.

The subject matter is treated in much the same manner in both the first edition[1] and this second edition. However, many changes have been made in addition to the incorporation of new material which has appeared since the publication of the first edition. In the preface the author states:

> . . . . A number of chapters have been entirely rewritten, especially those dealing with the mycorrhiza fungi and the soil as a medium for plant and animal parasites. A number of new chapters have been added, dealing with the rôle of microörganisms in the decomposition of organic matter in green manures and stable manures, in the formation and decomposition of peat and forest soils, and with the relation between plant growth and the activities of microörganisms in soil. To avoid any considerable increase in the size of the book a certain amount of condensation became necessary so as to balance the added material. This was accomplished by leaving out some of the text which did not bear directly upon the subject under consideration. Several chapters have been combined so as to avoid unnecessary duplication. . . . .

It is unfortunate that, in order to conserve space, it was also necessary to leave out the titles of papers in the references.

The following indicates the nature of some of the changes:

	FIRST EDITION	SECOND EDITION
Total pages	xxviii + 897	xxviii + 894
Text pages	843	829
Chapters	32	34
Chapters eliminated or combined with other chapters		4
Chapters added by expanding original material		6
Figures	77	83
Tables	119	127
Plates	19	15
Figures in plates	154	152
Books listed for reference	204	216
References in text	3,210	4,248

Although these figures do not indicate the large number of changes in reproductions, tables, and text it is quite apparent from the numbers of references

[1] For review of the first edition see *Soil Sci.* 23 (1927): 494–495.

that, even though the two books are practically identical in size, much material has been added in the new edition.

To those familiar with the first edition it seems sufficient to state that the new edition will be a valuable complement to it.

ROBERT L. STARKEY.